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Development and Applications of Gas Chromatography - Atomic Absorption Interface Instrumentation.

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DEVELOPMENT AND APPLICATIONS OF GAS CHROMATOGRAPHY-ATOMIC ABSORPTION INTERFACE INSTRUMENTATION

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DEDICATION

To my Mother and my Father for their belief in me;
they have waited a long time for this moment.

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FOREWARD

A selection of work appearing in this dissertation has been published in the following papers:

(1) "A Metal Specific Atomic Absorption Detector for Gas Chromatography-Its Use in the Determination of Lead Alkyls in Gasoline," J.W. Robinson, L.E. Viduarreta, D.K. Wolcott, J.P. Goodbread and E. Kiesel, Spectoscopy Letters 8(7), 491-507 (1975).

(2) "The Development of a Gas Chromatography-Furnace Atomic Absorption Combination for the Determination of Organic Lead Compounds. Atomization Processes in Furnace Atomizers," J.W. Robinson, E.L. Kiesel, J.P. Goodbread, R. Bliss and R. Marshall, Analytica Chimica Acta 92, 321-328 (1977).

(3) "Concentrations of Molecular and Organic Lead in the Lead in the Atmosphere," J.W. Robinson and E.L. Kiesel, J. Environ. Sci. Health A12(8), 411-422 (1977).

(4) "Studies of Interactions Between Tetraethyl Lead and Sea Water Using G.C.-A.A.," J.W. Robinson, E.L. Kiesel and I.A.L. Rhodes, J. Environ. Sci. Health A14(2), 65-85 (1979).

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ABSTRACT

It is being recognized that we are exposed to increasing numbers of poorly understood and potentially toxic substances within our environment.

To understand fully the human health effects and environmental impact of these hazards, complete chemical characterization or "speciation" studies of these hazards is necessary.

Once exposure to a toxic substance has occurred, the physical and chemical form will determine the length of time a compound will remain in the environment and the types of chemical reactions that will occur in atmospheric, aquatic, and soil environments. Physiological and toxicological effects are also dependent upon the chemical form and physical form.

This dissertation has been limited to heavy metal chemical hazards, and more specifically to lead and cadmium and their compounds.

A new atomic absorption (A.A.) detector for gas chromatography (G.C.) was developed. It was directly interfaced to a gas chromatograph through a pyrex transfer line. The detector exhibited the excellent specificity of atomic absorption while retaining the sensitivity of carbon furnace

atomizers. The G.C.-A.A. system permitted detection of different chemical forms of a given element.

The determination of lead alkyls in gasoline was chosen as a practical sample to demonstrate the G.C.-A.A. as an important analytical technique for characterizing mixtures containing volatile metal compounds. Unleaded gasolines were also analyzed for lead compounds.

It was discovered that the G.C.-A.A, could be utilized as a nonspecific detector for organic compounds with various functional groups.

A new modified G.C.-A.A. detector was designed and built. The purpose of the design was to improve the life-time of the resistance heated carbon element.

The evaporation of lead alkyls from gasoline was studied to determine the possible contribution of evaporating gasoline to atmospheric lead concentrations. The reactions of tetraethyl lead in sea water were also studied.

The reaction of cadmium and Vitamin methyl B_{12} was studied. A volatile cadmium compound was formed but the quantity formed was insufficient to characterize it completely.

The G.C.-A.A. system developed in this research is very sensitive and selective. It is ideal for speciation studies involving volatile metal compounds and complexes.

CHAPTER 1

INTRODUCTION

Great technological advancements have taken place in the last century. Man's knowledge of science and technology have grown at a phenomenal rate. In six and a half decades man has not only learned to fly but also has been to the moon and back.

Our technology is constantly striving to improve our very existence within our environment. Industries based on this new technology are producing a variety of products. Of particular interest is the chemical industry. New chemicals are being produced that are supposed to make our daily lives more convenient or more efficient. These varied products range from fertilizers and insecticides to synthetics and cosmetics to food and drugs.

With this expanding industry comes a new awareness of hazards. It is being recognized that we are exposed to increasing numbers of poorly understood and potentially toxic substances within our environment.

To understand fully the environmental impact of these potential toxins, two major components must be examined.[1] First, what are the toxicological effects to man and to other ecosystems? An understanding of the

chemical in question is necessary to answer this question. Second, what are the factors that determine the levels of toxic substances in the environment to which man and other ecosystems will be exposed? Such factors may be the production, use, and disposal patterns of toxic substances.

Once these questions are answered, rational steps can be taken to control the problem rather than relying upon uninformed emotional arguments to ban the use of a chemical. Without examining the advantages and disadvantages of a chemical's use, intelligent decisions cannot be made.

Man's environment is the complex matrix in which he lives. The environment consists of air, water, soil, and other biological systems. A primary concern of environmental impact is man's relationship to his environment and how it interacts with him. This can be directly translated into physical and emotional health.

A. ENVIRONMENTAL POLLUTION

A pollutant can be broadly defined as a contaminant. The term is usually reserved for harmful chemicals or harmful waste materials discharged into the environment such as the water (i.e., rivers, lakes, oceans, and their tributaries), atmosphere, or soil. It can also be used to describe the contamination of an ecosystem.

Because pollution is a very generalized term applying to any kind of contamination, this discussion has been limited to chemical contamination, and more specifically to

heavy metal pollution.

1. Air Pollution

Air pollution by heavy metal compounds can occur through man-made and natural processes. Mining and refining of heavy metals are major sources of airborne heavy metals. Other major sources of air contamination by metals and metal compounds are the burning of coal, fuel oil, or other fuels which contain metals. For example, the combustion of gasoline containing lead compounds is a principle source of atmospheric lead pollution.[2] Once a pollutant containing a heavy metal is airborne, it can settle out and contaminate soil, water, or biological systems.

It is convenient to consider pollution as divided into two fractions, (1) water soluble and (2) water insoluble fractions. There are then only two possible routes of contamination of the environment. (1) Direct contamination of soil and vegetation can occur as insoluble heavy metal compounds settle from the air and adhere to or are adsorbed onto surfaces. (2) The soluble form can leach into the soil where it can be absorbed by plant roots[3] or further be leached into water tables or streams.

Air pollution is a direct hazard to humans and animals through inhalation. This can be an especially major problem in the industrial work place. Air pollution hazards are not only confined to industry (stationary sources) but are also a problem in urban and suburban areas due to mobile

sources. The toxic effects of heavy metal air pollution will be discussed later.

In the industrial work place heavy metals can be volatilized by burning fuels or in smelting processes. Exposure of humans to heavy metals also occurs when volatile heavy metals are used improperly or without adequate protection. For example, at one time it was common practice for machinists to use mercury as a lubricant when machining hard metals.[4]).

In non-industrial urban and surburban areas, major sources of heavy metal air pollution are mobile sources, e.g., automobiles burning leaded gasolines.[2] Another mobile source of heavy metal pollution is cigarette smoking.[5-9] This source is becoming increasingly more important as more associated human health hazards are elucidated.

2. Water Pollution

Water can become polluted through the raining out of airborne pollution, both of man-made and of natural (e.g., volcanic activity and dust from arid zones) origin. Soil erosion and the leaching of hazardous materials from the soil are also routes by which water becomes polluted. A major source of water pollution is the direct discharge of a pollutant into a waterway.

Wastewater from the electroplating industry is a major source of aqueous cadmium pollution. Water pollution by mercury has also caused much concern in recent times. It has been found that bacteria in sediment can aerobically

and anaerobically convert mercury to the extremely toxic dimethyl form.[10]

The environmental impact of such water contamination can be severe. Humans and other animal forms can be affected by direct ingestion of polluted water depending upon its toxicological properties. Humans and animals are affected as the toxin is translated up the food chain.

3. Soil Pollution and Biological Effects

The soil has been directly polluted by chemical dumps and land fills. Contamination of soil and vegetation can occur as the insoluble component of air pollution adheres to or is adsorbed onto surfaces. There is no direct evidence of poisoning of the soil by the unchanged insoluble fraction. However through bacterial action and reactions with soil components, the insoluble fraction can be converted into a form that can be picked up by plants. Heavy metals can replace essential nutrients in plant metabolism.[3]

Soil around industries and highways has been shown to be contaminated with heavy metals. High levels of cadmium have been found in soil around industries utilizing zinc and cadmium up to distances of 8-10 miles before levels equivalent to surburban background levels are observed.[1] Soil up to 50 feet from the sides of highways have been highly contaminated with lead from automobiles.[2] Lead pollution has not been limited to areas adjacent to highways, but has been carried as far as the Arctic.[11]

The soluble pollution fraction can leach into the soil where it can be absorbed by plant roots[3] or further leached into water tables or streams. Once plant life is contaminated by these toxic metals, whether absorbed or adsorbed, the contamination can be translated up the food chain into other biological systems.

B. THE IMPORTANCE OF HEAVY METALS

Heavy metals have played a variety of roles throughout history. They have been used for their ornamental value (e.g., gold and silver). They have been used as pigments (e.g., cobalt blue). Correlations are being made linking exposure to metals and metal compounds and specific events. Lead and mercury have been recognized as toxins in the industrial workplace and as environmental toxins. Both chromium and arsenic have been found to cause dermatitis and cancer. Excess manganese can cause muscular disorders.

Some heavy metals regardless of chemical form are toxic to living systems. However the chemical form influences the degree of toxicity for a given element. For example, lead chloride and triethyl lead chloride are both toxic lead compounds but of the two, triethyl lead chloride is much more toxic. It can be seen therefore that the toxicological effects of a metal compound are related to its chemical form.

Once pollution by a toxic metal compound has occurred, the chemical form will determine the length of time a

compound will remain in the environment. The discussion in this dissertation will be limited to two elements and their compounds, lead (Pb) and cadmium (Cd).

In 1974, greater than 16% of the lead consumed in this country was utilized in leaded gasoline.[12] The automobile is considered a major source of lead input into the environment.[2] Soil, up to 50 feet from the sides of highways have been contaminated with lead from automobiles (i.e., from leaded gasoline). Leaded gasoline contains lead alkyls (tetramethyl lead [TML], trimethylethyl lead [TMEL], dimethyldiethyl lead [DMDEL], methyltriethyl lead [MTEL], and tetraethyl lead [TEL]) as antiknock additives. These lead alkyls are volatile and extremely toxic. Different brands of gasoline contain different proportions of these lead compounds. It is believed by some researchers that evaporating gasoline is a major source of atmospheric lead pollution.

Cadmium is a by-product of zinc production and has become important in the last 50 years. It is used extensively in the electroplating industry. Cadmium has been found in cigarette smoke. It is toxic and has been linked to various disease processes.

C. LEAD AND CADMIUM TOXICITY

Lead or cadmium poisoning can be acute or chronic. Each causes various generalized systemic manifestations including nasopharyngial irritation, cough, dyspnea, vomiting, diarrhea, insomnia, headache, dizziness, weight

loss, muscle and nervous disorders, and anemia. Both are known to accumulate in the liver, kidneys, and bones. There is no good indicator for the severity of exposure to these heavy metals. Symptoms and urinary excretions bear no relationship to the severity or duration of exposure. At best by monitoring such excretions, only a confirmation of absorption can be made.[13]

1. Lead Toxicity

In addition to the above symptoms, lead can effect several organ systems. Lead, however, has not been found to be mutagenic or teratogenic. Triethyl lead compounds have been shown to induce hypomyelination and to restrain myelin deposition and protein synthesis in developing rat forebrain. Prolonged exposure to lead and gasoline vapors have been shown to cause disorders of lipid metabolism in rabbits.[14] Lead has also been reported to decrease resistance to infections and modify pathways of detoxification and excretion.[15] Lead has a damaging effect on erythropoetic elements in bone marrow and upon erythrocytes.

2. Cadmium Toxicity

Cadmium, like lead, has a cumulative toxicity. It can induce hepatic[16] and renal[17-19] dysfunction. Cadmium replaces zinc in enzymes at high pH. There is a very strong linkage between cadmium exposure and hypertension. Cadmium can also interfere in carbohydrate

metabolism.[1] For many years it has been known that cadmium can cause tumors in experimental animals.[20, 21] Recently cadmium exposure has been correlated to an increased rate of prostatic cancer in humans.[22] Cadmium has also been related to anemia.[23]

3. General Toxicological Considerations

Volatile heavy metal compounds are potentially the most harmful chemical form of the elements. They readily contaminate the atmosphere. To fully appreciate the potential hazards of these heavy metals, it is necessary to perform speciation studies on them. The physical nature and chemical form will determine the solubility in water and biological fluids, and the types of chemical reactions occuring in atmospheric, aquatic, and soil environments. Physiological, pharmacological, and toxicological effects are also dependent upon the chemical form. The chemical form will determine the rate of absorption, distribution, biotransformation, physiological effects, and mode and rate of excretion.[24]

D. METAL SPECIATION STUDIES

1. Trace Metal Determinations

The importance of trace metal analysis has increased steadily in the last two decades. Conventional methods of analysis have consisted of wet chemical methods, if necessary including preconcentration techniques such as precipitation, solvent extraction, and evaporation. More

recently these techniques are sometimes followed by instrumental techniques of analysis (e.g., infrared spectroscopy, mass spectroscopy, ultraviolet spectroscopy, nuclear magnetic resonance spectroscopy, thermal analysis, electrochemical techniques, etc.). These are time consuming methods that involve elaborate and often complex techniques.

A standard practice, whenever trace metal determinations are required, is to do a determination of the total concentration of the metal of interest. Total lead is normally determined by atomic absorption or X-ray fluorescence. There are several standard methods used for total cadmium determinations: (1) dithizone colorimetric analysis, (2) atomic emission, (3) atomic absorption, (4) neutron activation, and (5) electrochemical methods. A total determination gives no indication of the chemical form.

There is an increasing interest in performing speciation studies. The long, involved techniques of the past (i.e., isolation and then complete characterization by a variety of determiantions) are giving way to new combinational techniques of analysis. The great resolving power of gas chromatography (G.C.) is being utilized. This separation technique is being coupled to specific detectors. These specific detectors include G.C.-mass spectrometry,[25] G.C.-electron capture,[26,27] G.C.-spectrophotometric techniques,[28] and G.C.-atomic absorption spectroscopy.[29-38]

2. Development of a Gas Chromatography-Atomic Absorption System

Several workers have made attempts to couple gas

chromatography and atomic absorption. In 1966 Kolb et al., reported the interfacing of a G.C. to a flame A.A. The technique had poor sensitivity.[29] Hey in 1971[30] and Gonzalez and Ross in 1972 developed a method for determining mercury alkyls. Both groups interfaced A.A. as a specific detector with G.C. Gonzalez determined trace mercury alkyls in fish tissue.[31] The Perkin-Elmer HGA 70 carbon furnace was modified by Segar to be interfaced with G.C. Segar analyzed lead alkyls but his instrument had a high molecular background and poor sensitivity (10^{-8} g/ul for Pb).[32] Lead alkyls in gasoline were also determined by Coker in 1975.[34] He directly coupled a G.C. to a flame A.A. The combined G.C.-A.A. system simultaneously developed by Robinson et al., had a sensitivity of 10^{-9} g/μL Pb.[33] It was a graphite furnace detector and will be discussed later. Later that year Chau et al., reported coupling a silica furnace A.A. to a G.C. to determine organo selenide compounds. By introducing hydrogen into the furnace he found he could improve his sensitivity.[35] Several other researchers have also utilized A.A. as a metal specific detector for G.C.[36-38] Most of these techniques involve an attempt to couple commercially available atomic absorption units (flame and nonflame atomizers) with gas chromatography.

3. Applications of Gas Chromatography-Atomic Absorption

A gas chromatography-atomic absorption system (G.C.-A.A.) has been developed in association with this

author's dissertation research. The G.C.-A.A. system is very sensitive and extremely selective and is ideal for monitoring volatile metal compounds.[33]

A study of leaded gasolines was first chosen to demonstrate the usefulness of the techniques. The G.C.-A.A. can also be used for air sampling analysis, where air samples are trapped out in a cold trap or on an adsorbent and placed in the G.C. A large portion of atmospheric molecular lead pollution is attributed to evaporating gasoline. A simple experiment was designed to determine lead concentrations in evaporating gasoline.[39]

In 1976, NATO Science Committee's Panel on Marine Sciences, in regard to a sunken cargo ship carrying tetraethyl lead (TEL), concluded that very little is known of the reactions of TEL and sea water.[40] Speculations of the effects ranged from "catastrophic" to "no effect." G.C.-A.A. is an ideal method for studying the kinetics of TEL in sea water.[41]

It was found that the atomic absorption detector could be used as a nonspecific detector for several functional groups.

E. METHYLATION OF CADMIUM WITH VITAMIN B_{12}

A common method of detoxification of chemicals and heavy metals in the body is by methylation. Several compounds are believed to be methylated in the liver and then removed from the body by respiration. Vitamin B_{12} is known to be a natural methylating agent which is involved

in metabolic methylations.[42,43] The G.C.-A.A. system is ideal for monitoring such reactions.

F. SUMMARY

Pollution of the environment by heavy metals is largely caused by humans. Cadmium is a by product of zinc production and has become important in the last 50 years. Lead has been known for centuries. It is represented among the so-called "old metals." A gas chromatography-atomic absorption detection system offers the sensitivity and selectivity of atomic absorption with the potential to be utilized as a specific detector due to the separation capabilities fo gas chromatography.

Several detection systems have been used as specific detectors.[44] Among them are electron capture, radioisotopic tracers, and mass spectrometry. The first two of the above techniques are sensitive but lack selectitity of atomic absorption as a detector. Similarly mass spectrometry lacks the sensitivity of atomic absorption as a detector.

A gas chromatography-atomic absorption system has been developed. It is very sensitive and is extremely selective. Because of its selectivity, G.C.-A.A. has advantages over other detection systems. G.C.-A.A. offers a combination system that is sensitive enough to detect low concentrations of sample while keeping sample handling to a minimum.

Gas chromatography as a separation technique is limited to volatile compounds. Volatile heavy metal compounds are

potentially the most harmful chemical form of the elements.[45-47] They readily contaminate the atmosphere.

CHAPTER 2

THEORY

A. GAS CHROMATOGRAPHY

1. History

In 1941, Martin and Synge developed liquid-liquid partition chromatography[48] while trying to separate amino acids. At this time Martin proposed the feasibility of using a gas as a mobile phase rather than a liquid. He had described gas-liquid chromatography. The first successful gas chromatographic separation was not realized until 1951 by James and Martin. The effluent gas was determined by an automatic recording burette.[49]

From this early beginning gas-liquid chromatography as an analytical field has mushroomed. Major advances have come in the development of improved detector systems (These will be discussed in greater detail later).

Routine support coated gas chromatographic columns are still made the same as Martin's. A thin layer of non-volatile solvent is held on a solid support and packed into a tubular column. In 1956, Golay advanced gas chromatography with the introduction of coated capillary tubes as chromatographic columns.[50, 51] The new capillary columns have improved separation efficiency and decreased the sample size required for analysis.

2. Theory

Gas chromatography (G.C.) is a physical method of separation based on a differential migration process. Separation efficiency is dependent upon the following: (a) the dimension of the zone from which migration proceeds, i.e., sample size; (b) a difference in rates of migration of the individual components; and (c) the length of the migration path. Separation is accomplished by partitioning a sample between a mobile gas phase and a stationary phase.

In gas-liquid chromatography a thin film of nonvolatile liquid (substrate) is held on a solid support. Gas-solid chromatography uses a solid adsorbent as the stationary phase. The net flow rate of a compound through a column is controlled by (a) the fraction of solute in the mobile phase and (b) the partition coefficient of the compound between the mobile and stationary phases which determines the time the compound will spend in the stationary phase.

If it is assumed that the entire sample is introduced onto one theoretical plate as a single plug, then the number of theoretical plates is a measure of column efficiency.[52] (Equation 1)

$$N = 16\left(\frac{x}{y}\right)^2 \qquad (1)$$

where:

N = number of theoretical plates

x = distance between the point of injection and the peak maximum

y = peak width

The efficiency of a column to distribute a solute in a Gaussian type distribution can best be described by the height equivalent to a theoretical plate (HETP or H). (Equation 2)

$$H = \frac{L}{N} \qquad (2)$$

where:

L = length of the column

N = number of theoretical plates

Van Deemter et al., have related the column efficiency to several important column parameters.[53] (Equation 3)

$$HETP = A + \frac{B}{\bar{u}} + C\bar{u} \qquad (3)$$

where:

A = eddy diffusion term, represents packing and multiflowpath constants. In open tubular columns, A = 0.

B = longitudinal diffusion term, describes the band spreading due to molecular diffusion of the solute.

C = resistance to mass transfer from the gas phase to the liquid phase, and vice versa.

$\bar{u}$ = average linear velocity of the carrier gas.

There are several general required properties of compounds to be chromatographed. The compound must be volatile. Every compound has a unique temperature versus vapor pressure plot. A compound may have a higher vapor pressure than another at one temperature but a lower vapor pressure at another temperature. Because most compounds travel through a G.C. column at a temperature lower than the com-

pound's boiling point, the vapor pressure at the column temperature is the more important. Therefore, volatility is dependent upon the temperature of the column. Compounds with high intermolecular forces such as charged or highly polar species cannot be chromatographed due to low volatility. Volatility is also decreased by large dipoles, polymerization and hydrogen bonding.

A compound must be relatively stable to be chromatographed. If the compound of interest reacts with any component of the G.C., qualitative and quantitative work becomes very difficult. Many compounds will react with traces of oxygen in the carrier gas or will decompose at elevated temperatures. This is a very important consideration when working with organometallic compounds because of the high reactivity of most organometallic compounds. Another problem that is encountered is the sample irreversibly interacting with the substrate or with other components in the sample mixture to be separated.

Special properties of compounds can also be used to advantage (e.g., the ability to form complexes). With halogen specific detectors, halogenated analogues can be made to enhance sensitivity. The ability of heavy metals to form complexes can also be used in gas chromatography since many are volatile complexes.

Among the chelating agents used to form volatile metal complexes are the following: acetylacetonate, fluro-carbon β-diketonate chelates, tri-and hexafluroaceton-

ates.[54-59] Several metal halides are volatile and can be chromatographed.[55]

3. Detectors

Katharometers (or thermal conductivity detectors) have been used for many years and have been exhaustively studied.[60] They remain one of the most popular detectors even today.

Many highly sensitive and selective detectors in gas chromatography have been developed since 1957. The flame ionization detector (F.I.D.) was reported in 1958 by Harley, Nel, and Pretorius[61] and by McWilliams and Dewar.[62] The F.I.D. was considerably more sensitive than any previously available detector. Lovelock introduced the electron capture detector (E.C.D.).[63] The E.C.D. was a highly sensitive and selective detector ideal for detection of halogenated compounds, especially pesticides which are often chlorinated hydrocarbon.

Other detectors used in gas chromatography are the noble gas detector (or beta-ray detector), ultrasonic detector, and specific element detectors (halogen and phosphorus detector or halogen specific F.I.D.). When choosing a detector, one must consider the following: the sensitivity, the selectivity, and whether the detector is destructive or nondestructive.

4. Special Detectors

Gas chromatography is a very powerful separation technique and can be interfaced with several analytical

systems.

Flame ionization (F.I.D.) and electron capture (E.C.D.) detectors are very sensitive (10 ppb and 0.01 ppb respectively). The F.I.D. is non selective and suffers from many interferences. The E.C.D. is sensitive and selective but is expensive and requires an A.E.C. license to maintain the detector. The E.C.D. is also severely affected by column bleed.

B. ATOMIC ABSORPTION

1. Basic Principles

Atomic absorption is defined as "the study and measurement of radiant energy by free atoms."[64] Walsh introduced atomic absorption in 1955.[65] Molecules or ions are converted into free atoms and then the absorption of radiation by these free atoms is measured.

The absorption of radiation by free atoms follows a Beer's law-type relationship in that absorption has a logarithmic relationship to concentration. Because the population of free atoms in the light path of an atomic absorption atomizer is nonhomogeneous, a more accurate relationship involves absorption and the number of free atoms rather than concentration.

The total absorption is proportional to the number of free atoms and the oscillator strength of the absorption line. (Equation 4)

$$\int_0^\infty K\nu \, d\nu = \frac{\pi e^2}{mc} N_o f \qquad (4)$$

where:

$K\nu$ = absorption coefficient at frequency ν

e = charge of an electron

m = mass of an electron

c = speed of light

N_o = number of absorbing atoms

f = oscillator strength of the absorption line

Because the oscillator strength is a fixed physical quantity for a given absorption line, sensitivity can be improved by choosing a resonance line with a strong oscillator strength. Though the oscillator strength is the limiting factor for the sensitivity of atomic absorption, for a given element at a given frequency, the size of the absorption signal is determined by the number of free atoms produced in the atomizer. It follows that the efficiency of the atomization process will determine the practical sensitivity.

2. Atomic Absorption Atomizers

The most convenient method of resolving a sample into its component elements (atomization) is thermal decomposition. Flames were first utilized for this purpose. The total consumption and Lundegardh burners were the most widely used. Because of the instability and reactive nature of a flame, resistance heated carbon furnaces were introduced. Flame atomizers yield a sensitivity of approximately 10^{-7} grams,[66] within the part per million concentration

range. Theoretical calculations show that 10^{-16} grams of an element (10^{7} atoms) should give a 1% absorption signal.[67]

To further increase sensitivity, there must be an increase in the number of atoms available to absorb. Resistance heated graphite is a much more efficient atomizer than a flame. L'vov in 1961 reported the first effective nonflame atomizer.[68] This atomizer consisted of a carbon tube lined with tantalum foil. The furnace was very sensitive but lacked both accuracy and precision. In 1969 at the Atomic Absorption Conference in Sheffield, England, West introduced the carbon filament atomizer[69] and Robinson introduced the "quartz T" atomizer.[70]

The carbon filament atomizer consisted of an electrically heated carbon filament. The sample was loaded directly onto the filament. A very rigorous heating program, to dry, ash, and then atomize the sample, had to be developed in order to obtain reproducible results.

Another carbon furnace atomizer, the Massman furnace, was developed for commercial use by Perkin-Elmer Corporation.[71, 72] The atomizer consisted of a graphite tube that was electrically heated. The sample was loaded into the center of the tube. Again, a carefully controlled temperature program had to be used to obtain reproducible results.

The West and Massman atomizers were subsequently adapted for use in commercial atomic absorption spectrophotometers. Both atomizers, however, suffered from the

severe sample loss of volatile metals that occurred during the temperature program before atomization. This disadvantage will be discussed in greater detail later.

The "quartz T" had a carbon bed in one arm of the "T." The carbon bed was inductively heated by a R.F. generator and was kept at atomization temperature throughout the determination. The sample was introduced directly onto the carbon bed where atomization occurred. The free atoms from the sample were then swept into the light path where optical measurements were made. Unlike the carbon filament and Massman atomizers, the "quartz T" was not limited to liquid samples. Solid and gas samples could also be analyzed.

The "quartz T" did not suffer from the problems associated with temperature programed atomization since atomization and optical measurements were continuous processes. There were, however, two distinct disadvantages. (1) Because of size and because an R.F. generator was used to heat the atomizer, it was not readily adaptable to commercial instrumentation. (2) The maximum atomization temperature that could be attained was 1500°C which is the melting point of quartz.

In 1974 Robinson and Wolcott reported a new electrothermally heated carbon atomizer, a carbon "hollow T".[73] The "hollow T" atomizer (Figure 1) had the same advantages as the "quartz T" plus it could attain high temperatures (∿3000°C). At temperatures greater than 2000°C the carbon

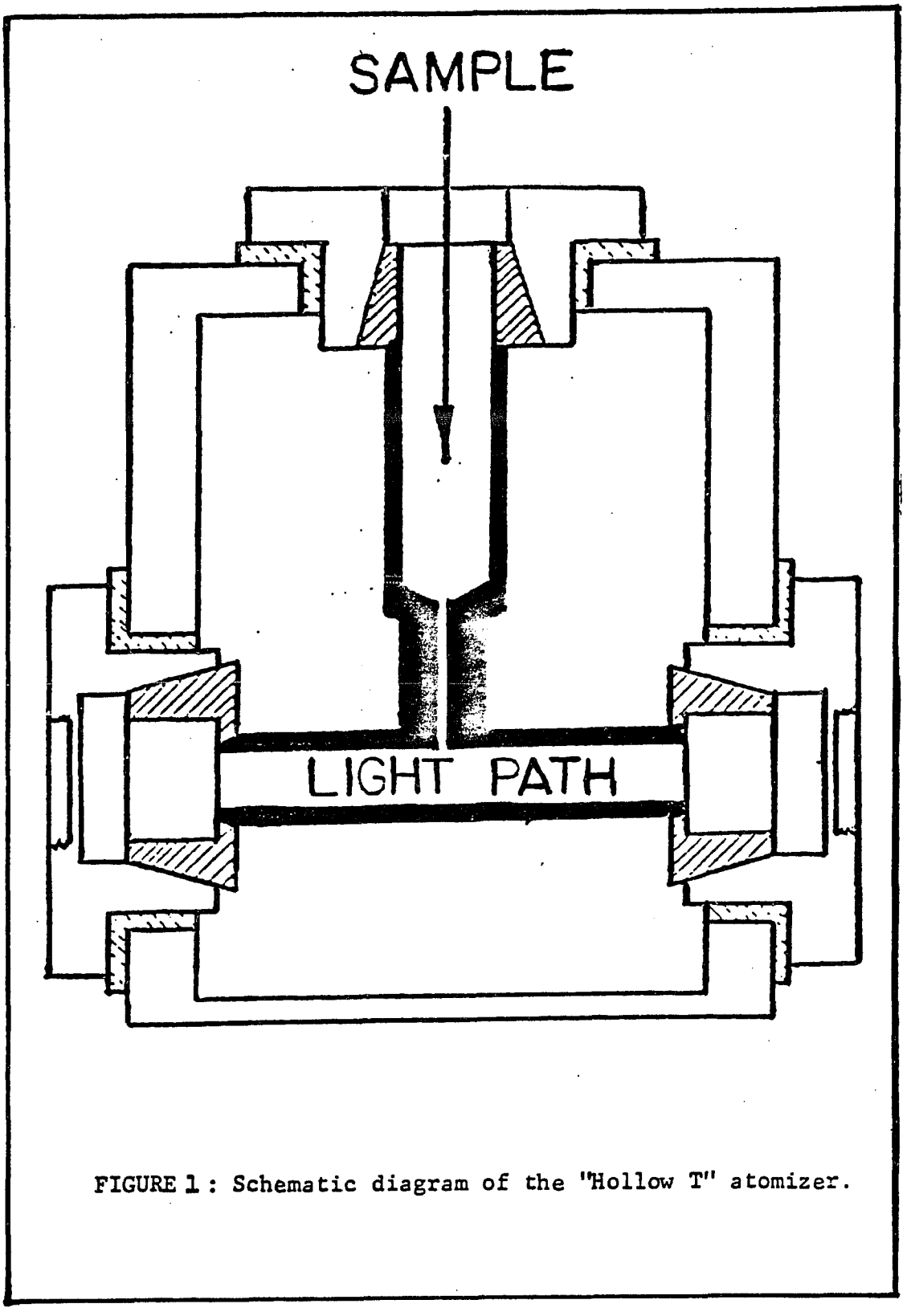


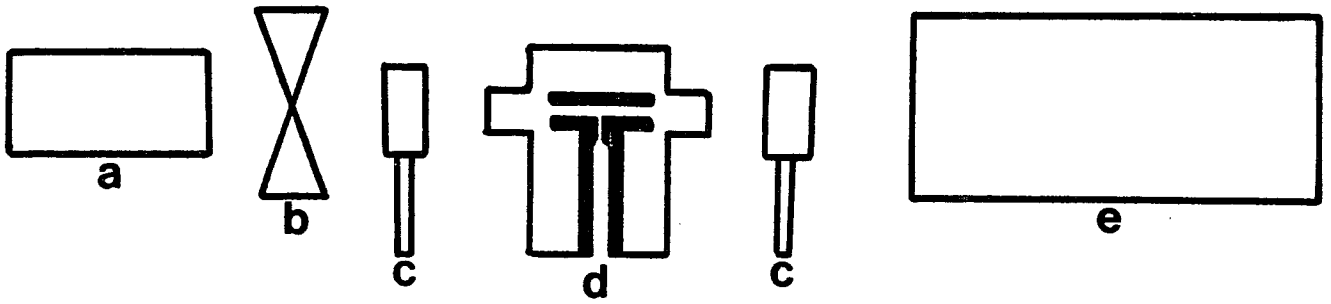
FIGURE 1 : Schematic diagram of the "Hollow T" atomizer.

piece was cleaned up rapidly. The "hollow T" atomizer gives very efficient atomization and requires inexpensive instrumentation. A reduced, modified version of the "hollow T" was used as a gas chromatography detector in this dissertation research.

3. Optical Systems

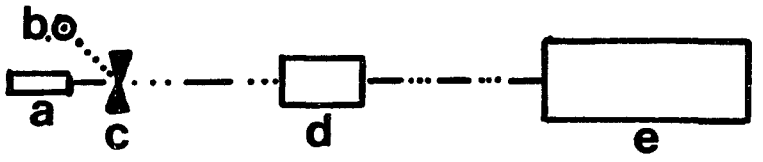
The atomic absorption spectrophotometer used in this research is essentially the same procedurally as a single beam absorption photometer (Figure 2). The instrumentation consists of a light source, a modulator, an atomizer, a monochrometer and read-out system.

The two most commonly used optical systems in commercial instruments are a single beam system and a pseudo-double beam system (Figure 3). In both systems a deuterium lamp can be incorporated into the optics for simultaneous background correction (Deuterium background correction will be discussed later). In a single beam system the radiation from the hollow cathode lamp and the deuterium lamp is modulated and alternately directed through the sample. The molecular absorption is then electronically substracted from the total signal leaving only the net atomic absorption signal. In the pseudo-double beam system, the radiation from the hollow cathode lamp is split by a beam splitter which alternately directs radiation along the reference path and then the sample path. Radiation from the deuterium lamp is similarly split. The



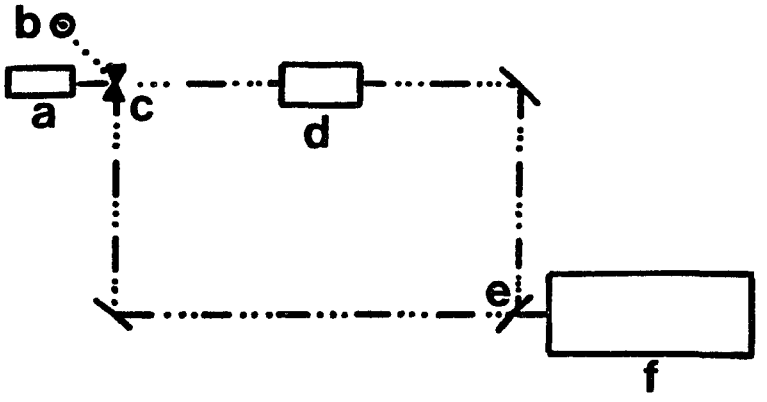
a. Hollow Cathode Lamp
b. Chopper
c. Lenses
d. Atomizer Detector
e. Monochrometer

FIGURE 2: Gas Chromatography-Atomic Absorption Optical System



Single Beam A.A. System

a. Hollow Cathode Lamp
b. D_2 Lamp
c. Chopper
d. Atomizer
e. Monochrometer



Double Beam A.A. System

a. Hollow Cathode Lamp
b. D_2 Lamp
c. Chopper, Beam Splitter
d. Atomizer
e. Beam Recombiner
f. Monochrometer

FIGURE 3: Single and Double Beam A.A. Optical Systems

reference and sample beams are then recombined and continue through the monochrometer. In this system not only is simultaneous background correction made, but also drift from unstable radiation sources is corrected.

4. Light Sources

a. Hollow Cathode Lamp

The natural spectral line width of an atomic absorption resonance line is approximately 10^{-4}Å. Doppler effects and Lorentz (pressure) broadening all tend to increase the line width to approximately 0.02 Å depending on the wavelength of the resonance line and temperature.[64] A very narrow emission line is required from the light source in order to observe a discernible absorption signal without sophisticated electronic equipment. A hollow cathode lamp is used for this purpose. The lamp consists of an anode, a cathode made of the element of interest and an inert filler gas (Figure 4). The inert filler gas is ionized at the anode and attracted to the oppositely charged cathode where excited metal atoms are sputtered into the gas phase. As the excited metal atoms return to the ground state, they emit characteristic wavelengths of radiation. A spectra of emission lines of both the filler gas and the cathode material is emitted from the hollow cathode lamp.

The intensity of the lamp is dependent upon the efficiency of the sputtering process. This directly relates to the energy and pressure of the filler gas. Broadening of the emitted spectral lines occurs due to Doppler

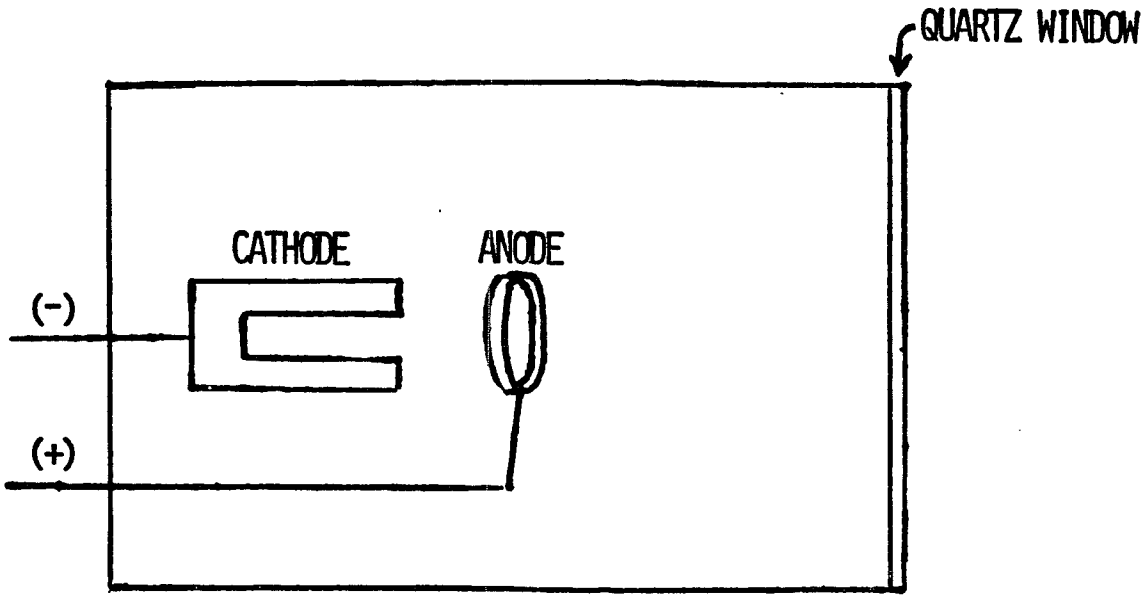


FIGURE 4: Schematic diagram of a Sealed Hollow Cathode Lamp

and Lorentz effects. Lamp intensity is also decreased due to self absorption or line reversal in hollow cathode lamps of volatile metals. As the population of unexcited or ground state atoms form a metal cloud in front of the cathode, they will absorb some of the emitted radiation. This absorption will distort the net emission signal (Figure 5) and will remove the most easily absorbed center of the line.

These problems mainly occur in sealed hollow cathodes lamps. By using a demountable hollow cathode lamp, these problems are decreased considerably. The demountable hollow cathode lamp (Figure 6) has two very important advantages:

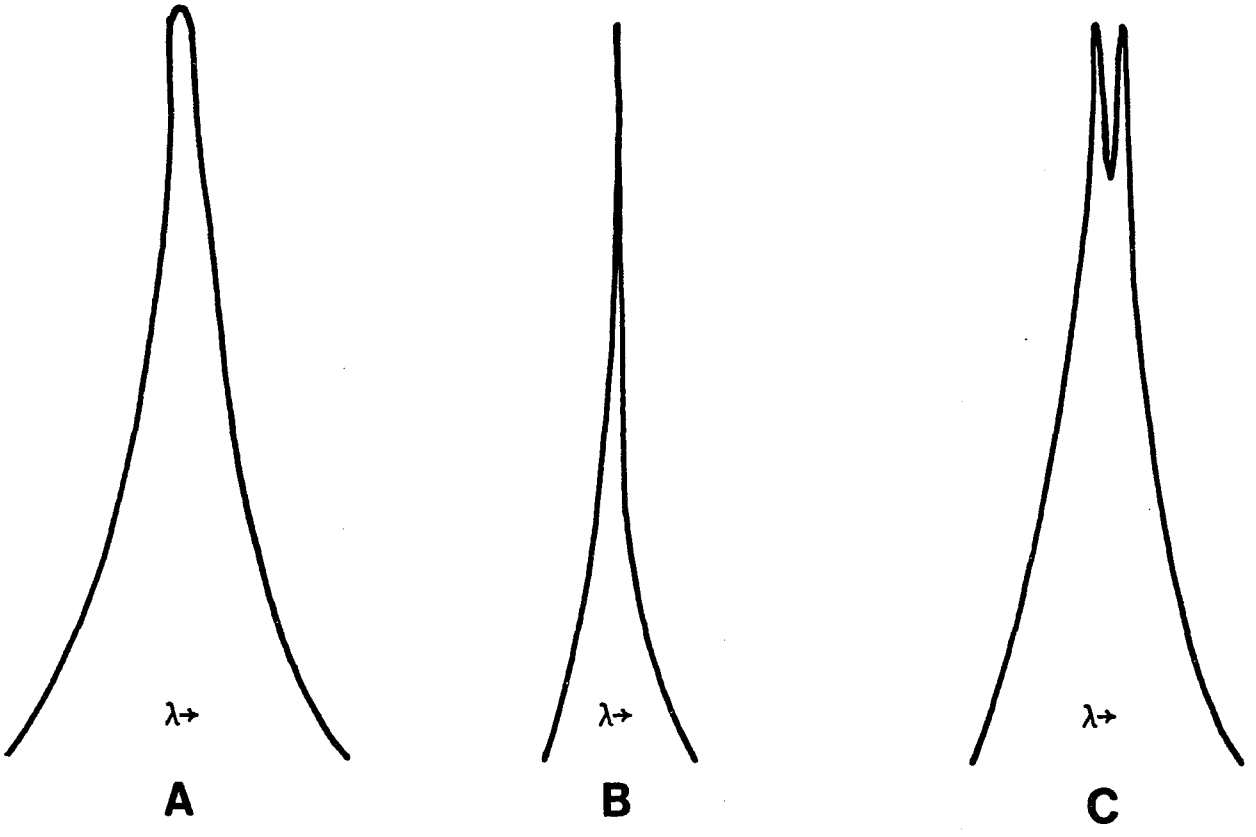
(1) the inert filler gas constantly purges the system and self absorption is neglible. This also allows the use of higher lamp currents, hence increased lamp intensity.

(2) the cathode can be replaced in a few minutes by a cathode of another element. From a practical point of view, this saves the expense of having to buy numerous hollow cathodes and also saves time.

b. Background Correction

When organic and inorganic molecules are introduced into an atomic absorption atomizer, decomposition may not be complete. Undecomposed fragments absorb over a wide wavelength range. When this includes the atomic absorption wavelength, background correction must be employed to compensate.

The simplest way to compensate background absorption is to make a blank solution. The blank solution should



A= shape of spectral line emitted by hollow cathode
B= shape of spectral energy band absorbed by cool atoms in a hollow cathode
C= shape of net signal emerging from a hollow cathode

FIGURE 5: Distortion of the Spectral Line Shape in a Hollow Cathode Lamp

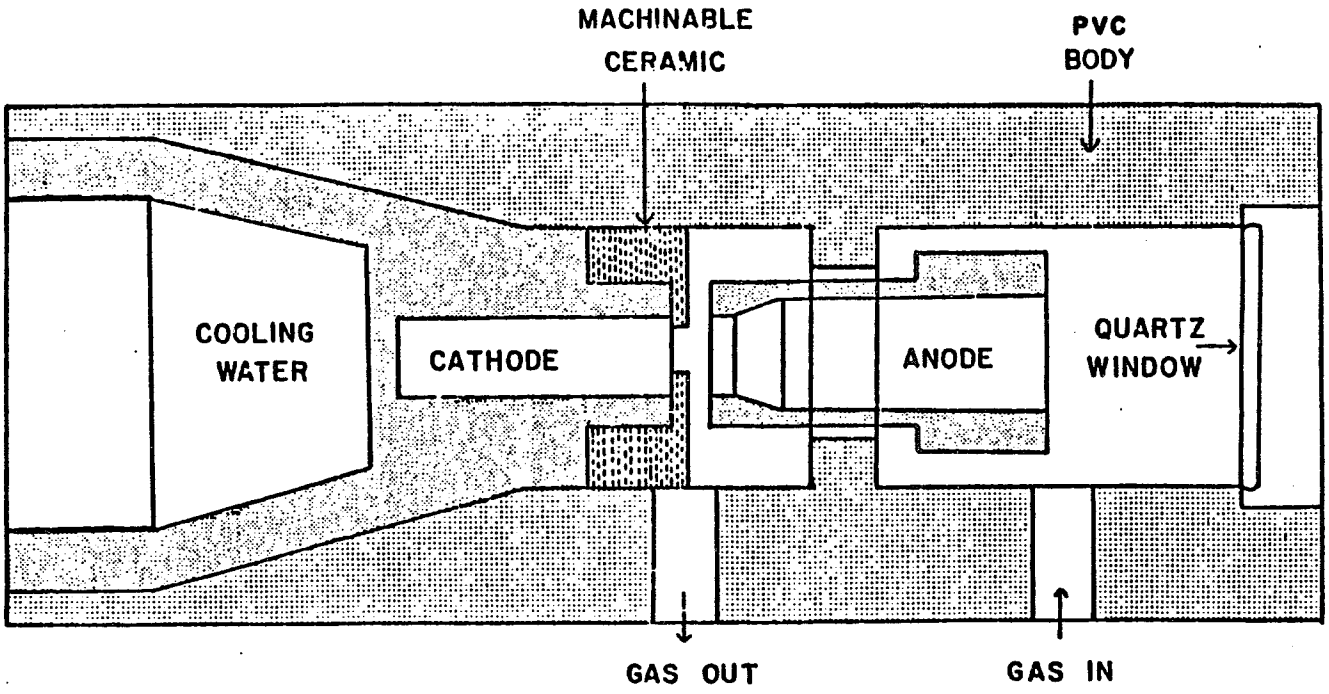


FIGURE 6: Demountable Hollow Cathode Lamp

contain the same matrix as the sample but should exclude the element of interest. The difference in absorption signals between the sample and the blank is assumed to be due to the element being determined.

There are several instrumental methods used for molecular background correction. These techniques utilize a radiation source that either is not absorbed by the element of interest or if absorbed by the element of interest the atomic absorption signal is negligible. Therefore only the molecular absorption is detected.

1) Background Correction Using the Two-Line Method[74]

Compensation of background by the two-line method uses a non-resonance line which is an emission line of the hollow cathode lamp that is not at an absorption wavelength of the element being determined.

The atomic absorption signal at the resonance line consists of the atomic and molecular absorption, whereas the absorption signal at the non-resonance line is only due to molecular background. The difference between these two signals is the net atomic signal.

This method requires that two measurements of the sample be made. If the measurements are not carried out simultaneously it must be assumed that conditions remain constant between measurements.

2) Background Correction Using a Continuum Light Source[64,74,75]

The second instrumental method for background correction uses a continuum light source, usually hydrogen or deuterium. Assuming the spectral line width falling on the detector is 1 Å and the absorption line width is 0.02 Å or 2% of the total falling on the detector, the contribution of the atomic absorption line to this method of background correction is negligible.

This method of background correction requires that the hollow cathode lamp be replaced with a continuum light source. It is assumed that the continuum light source is placed in the system without changing the optical path.

Some commercial instruments have incorporated a deuterium lamp into a double beam optical system (Figure 3). Light from the continuum and the hollow cathode lamps alternately pass through the atomizer and into the monochrometer. The difference in the signals is sorted electronically and the net signal is the atomic absorption signal.

3) Background Correction Using the Zeeman Effect

The third instrumental method of background absorption correction uses the Zeeman Effect.[64,76] The hollow cathode light source is split into two lines by the Zeeman effect. These two lines are shifted from the original unshifted resonance line which disappears. The unsplit radiation is at the resonance line and atomic and

molecular absorption occurs. The Zeeman-shifted radiation is absorbed by the molecular background but not by the atomic element of interest. The difference between these two signals is the net atomic absorption signal.

5. Detector Readout System

In addition to the light source and the detector, a detector-readout system is required to complete the atomic absorption system. The detector-readout system usually consists of a monochrometer, photomultiplier tube, amplifier and recorder. This subsystem must have a sufficiently fast response to measure the absorption of radiation for the brief time that free atoms are swept through the light path.

Detector response time has frequently been a problem in commercial units originally designed for flame atomizers that are being coupled to furnace atomizers. The amplifiers and readout system for flame atomizers are designed for much slower response times than required for furnace atomizers and are totally unsuitable for such purposes. The data from such systems is more a measure of response times than metal concentrations.

6. Modulation of Equipment

The atomic absorption equipment must be modulated. During the atomization process free atoms are formed and are distributed between the ground state and the excited state according to the Boltzmann distribution. The excited

atoms can undergo a transition to the ground state emitting a photon of the same wavelength at which they absorb (i.e., the resonance line). This presents a problem when measuring absorption by ground-state atoms. Because radiation from the atomizer is continuous, by modulating the light source (either mechanically or electronically) and adjusting the detector to respond only to a modulated signal, absorption of radiation from the light source can be measured without interferences from extraneous light.

7. Interferences in Atomic Absorption

There are essentially only three interferences encountered in atomic absorption;[64] (a) molecular interference is any broad band absorption at the same wavelength as the atomic resonance line, (b) atomic (spectral) interference is any element that absorbs at the same wavelength being measured (this is a theoretical possiblility though it has not been observed), and (c) chemical interference is related to the chemical form of the sample and indirectly effects the atomization efficiency, and therefore the total free atom population from a given sample concentration.

8. Atomization Processes in Carbon Atomizers

To understand the advantages of the various atomizer designs, the atomization process in carbon atomizers must be understood. The formation of atomis is a very fast process and is difficult to examine. A mechanism for the production of atoms in a graphite furnace has been proposed

based on the reaction; $MO(s) + C(s) \rightarrow CO(g) + M(g)$.[77] There are many variables affecting atomization efficiency (i.e., the number of free atoms formed) and analytical measurement. It must also be remembered that the atom population never reaches a steady state. To control atomization efficiency, the variables affecting the rate and degree of atomization must be controlled. Most atomizers have a three step atomization process: (1) evaporation of the solvent; (2) ashing the sample at an increased temperature; and (3) atomization.

Depending on the physical form of the carbon rod or tube, liquid samples diffuse to a lesser or greater extent into the carbon. If a layer of pyrolytic carbon is deposited on the surface of the carbon tube, liquid diffusion into the carbon will be minimal and atomization will be relatively rapid. When the liquid sample diffuses into the carbon, evaporation, ashing and atomization steps are slowed down. This is because the sample must diffuse out of the carbon.

The chemical form of the sample strongly influences ashing and atomization. Chemical interferences, which can lead to serious errors, can be partially overcome by rigidly controlling the atomization process, i.e., rate of heating, temperature and time. Accurate, reproducible results can be obtained from pure solutions. However, controlling all of the variables when working with real samples that are not completely characterized is virtually impossible.

Electrical resistance of the carbon tube varies over a period of time with extended use. This is a source of error with standardized atomization programs. Though the atomization program remains constant, as the carbon ages, different atomization temperatures and rates of atomization are achieved.

Another problem with programed atomization is that optical measurements are only made during the atomization step and not during the evaporation or ashing steps. Sample can be lost due to volatilization in the early stages of the program leading to erroneous, inaccurate data. Though the data may not be accurate, precise and reproduceable results can be achieved under strictly controlled conditions. When analyzing real samples, chemical interferences and matrix effects can cause error. Because the processes never reach equilibrium, these errors exist even when precautions are taken to match the samples and the standards used.

As previously mentioned, Robinson's "quartz T" was presented at the Atomic Absorption Conference in Sheffield, England, in 1969. Because atomization occurred in a carbon bed outside of the light path, the atomizer could remain hot at all times. The "hollow T" type atomizers were designed in order that higher atomization temperatures could be reached.

The atomizer remains at atomization temperatures (>2000°C) while in use. The decomposition and atomization

occurs outside of the light path. Once atomization occurs, the free atoms are swept into the crosspiece (light path) where optical measurements take place. Decomposition is fairly rapid. Because a finite amount of time elapses from the time the sample enters the atomizer to the time atoms enter the optical light path, decomposition virtually eliminates chemical interferences. Most chemical interferences are caused by the varying rates of atomization of different compounds rather than the prevention of decomposition. The "hollow T" atomizer is far superior to any commercially available atomizer in terms of atomization efficiency, sensitivity, reduction of molecular background, ability to introduce a variety of samples (i.e., solid, liquid and gas samples) and simplicity of design. The "hollow T" type atomizers circumvent the many problems that occur in commercial atomizers.

9. Atomic Absorption Detector for Gas Chromatography

The atomic absorption detector for gas chromatography described in this research is a modified "hollow T". The atomizer was reduced in size and the inlet was modified to accept a transfer line for direct interfacing with the gas chromatograph (Figure 7).

The atomizer is left hot at all times. The effluent from the gas chromatograph enters the base of the atomizer. Decomposition and atomization occurs in the base. The atoms then flow into the crosspiece which is the optical light path. Here analytical measurements are made.

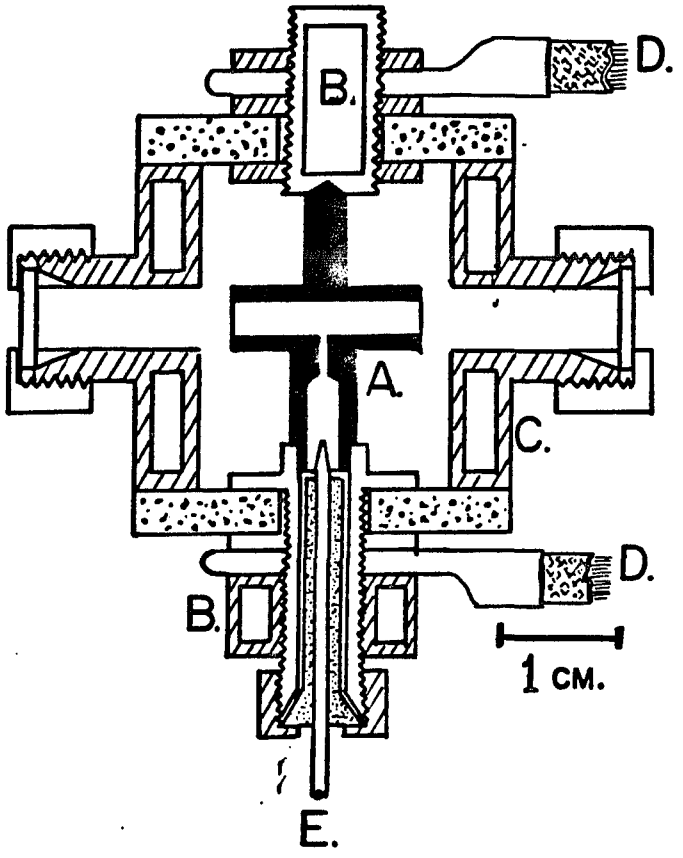


FIGURE 7- Flameless Atomic Absorption Detector

A. Carbon resistance element
B. Water-cooled electrodes supporting resistance element
C. Water-cooled atomizer housing
D. Welding Cables from power supply
E. Stainless steel capillary transfer line from gas chromatograph

This system has several advantages. The solvent is separated from the metal-bearing compounds by the gas chromatograph eliminating the need for an evaporation step. The gas chromatograph separates the metal-bearing compounds from the other sample components which eliminates the problem of matrix effects. The effluent enters the detector over a period of seconds allowing ample time for complete decomposition and atomization.

The major disadvantage of the technique is the requirement that the sample must be volatile. This disadvantage is also an advantage in that difficult to analyze volatile samples can be easily analyzed using this technique. Lead alkyl determinations in gasoline is a prime example. Because of the selectivity of atomic absorption and the separating ability of gas chromatography, gas chromatography-atomic absorption can selectively, with specificity, determine the lead alkyls in gasoline without interference from the hundreds of compounds in the sample matrix.[33]

10. Sensitivity of a Gas Chromatography-Atomic Absorption System

The sensitivity of atomic absorption is defined as a 1% absorption signal (0.004 absorbance units). The detection limit by convention is the smallest quantity of sample that will give a signal twice the noise level. When speaking of the sensitivity of a G.C.-A.A. combination, peak area must be taken into account. Peak area is directly related to the number of free atoms in the light path

(i.e., atomization efficiency). Peak broadening will tend to decrease the relative sensitivity of the instrument for a given component of a sample due to the limitation of the required 1% absorption signal required by A.A. It is therefore important to consider the atomic absorption detector as any other G.C. detector when determining sensitivity. The peak height is a product of the metal concentration and the resolution of the G.C. column. The definition of sensitivity as that concentration which results in 1% absorption is unrealistic. Sensitivity measurements are based on peak area data.

Gouw[78] has defined the definition of sensitivity for G.C. as the change in detector response divided by the change in concentration of the sample. (Equation 5)

$$S = \frac{R}{Q} \qquad (5)$$

where:

S = sensitivity

R = detector response

Q = quantity of sample

When the noise level is taken into account, where R_n is the maximum deviation around the average baseline, then the minimum quantity of sample that can be detected is Q_{min} Q_{min} is defined as twice the noise level divided by the sensitivity. (Equation 6)

$$Q_{min} = \frac{2R_n}{S} \qquad (6)$$

where:

Q_{min} = minimum detectable quantity

R_n = noise level

S = sensitivity

It is important to remember that the sensitivity of atomic absorption is defined as a 1% absorption signal. When determing absolute sensitivity of the system, the detector response with a peak height equal to 1% absorption must be used as the limiting factor. The sensitivity of the G.C.-A.A. for a given element is dependent upon the chemical form, the retention time, and the peak area.

CHAPTER 3

EXPERIMENTAL

A. INSTRUMENTATION

A serious problem in analytical chemistry is error introduced in the multiple handling of samples. The ideal analysis consists of a one step operation where a sample is placed inside an analyzing instrument and is completely characterized. Unfortunately, this type of elemental analysis rarely occurs. A typical analysis consists of (1) collection of the sample, (2) preparation of the sample for analysis (e.g., dissolution), (3) separation of the sample components from the sample matrix, and (4) qualitative and quantitative analysis.

The G.C.-A.A. system described in this paper is an attempt to come one step closer to the ideal analytical system. By directly interfacing a separation method with a sensitive spectroscopic method like atomic absorption, sample handling is reduced. Therefore the error of analysis is decreased.

To understand the potential of a combination analytical system like the G.C.-A.A., the advantages of the component systems must be examined. Atomic absorption has the

sensitivity capabilities to detect ultratrace concentration levels of metals. Sensitivity has been improved through more stable and intense light sources. Sensitivity has also been improved by detectors with increased stability. With double beam methods, signal locking devices, and interfacing of instruments with micro-processors, sensitivity can be further increased.

Gas chromatography is a very powerful analytical tool for separation. It provides a method of separating components from a complex sample matrix. It is a rapid and easy method of determining the minimum number of components in a mixture. It can be used to determine impurities in a substance, follow the progress of kinetics of a reaction, and by comparing retention volumes of a substance with a known quantity of a substance, qualitative and quantitative determinations can be conducted. Two requirements for a compound to travel through a G.C. column are that the compound must be volatile at the column temperature and that the compound must be stable at the temperature necessary for the production of the vapor phase.

The combined G.C.-A.A. system described in this paper has the separation potential of G.C. and the analytical selectivity and sensitivity of A.A. There are very few spectral interferences. Techniques are available to correct any molecular background absorption that may occur.

The G.C.-A.A. is a valuable technique for speciation studies. It compares well with other combined techniques

(e.g., G.C.-M.S., G.C.-I.R., etc.) used in speciation studies. Very often these other combined techniques lack the selectivity of G.C.-A.A.[55] For example, when G.C.-M.S. is used as a specific detector for lead, the Pb-207 isotope is monitored. Interference is often encountered from ions of polycyclic aromatic hydrocarbons that have fragments of the same mass.

The practical applications of the instrument were demonstrated by making the detector initially specific for lead and then later specific for cadmium compounds. These two elements were of interest because of their environmental impact and health hazards.

The G.C.-A.A. described in this dissertation is rudimentary in construction. The results show the great potential for G.C.-A.A. With several minor modifications sensitivity and reproducibility could be greatly improved.

1. The Gas Chromatograph

A Microtek G.C. 2000-R series gas chromatograph was used in this series of experiments. It was a very versatile instrument and readily lent itself to modifications with modular components. It had a large exterior frame with many vacant spaces inside the instrument which allowed the mounting of detectors or control electronics. Before the interfacing of this instrument with atomic absorption, it had been modified to accept an U.V. fluorescence detector.[79] The original instrument was a dual column with both thermal conductivity and flame ionization

detectors. The instrument contained a multiple gas flow system, a temperature programer and an electrometer. The electrometer was replaced with the detector read-out system for the atomic absorption detector which is described later.

Pyrex glass liners were made to replace the metal liners of the injection port. Reactive compounds are less likely to decompose on a hot pyrex surface than a hot metal surface. Metal surfaces are known to catalyze the decomposition of some compounds. This is particularly true of organometallics.

The temperature programer was repaired and the oven heating elements were replaced. The new heating elements were wound from 16 gauge nichrome wire.

2. The Atomic Absorption Detector

The atomic absorption detector was a modified and much reduced version of the "hollow T" atomizer. The detector consisted of a water cooled brass jacket (Figure 7). The resistance heated carbon element (Figure 8) was connected to two water cooled electrodes. The lower electrode was hollow to allow the G.C. effluent access to the atomizer. The G.C. carrier gas also served as the detector purge gas. The optical light path was made with quartz windows. Teflon washers were used to seal the windows in place and protect them from their metal supports.

Power to heat the carbon electrode was controlled by a 10:1 stepdown transformer that was fed by a 135V-15A auto-

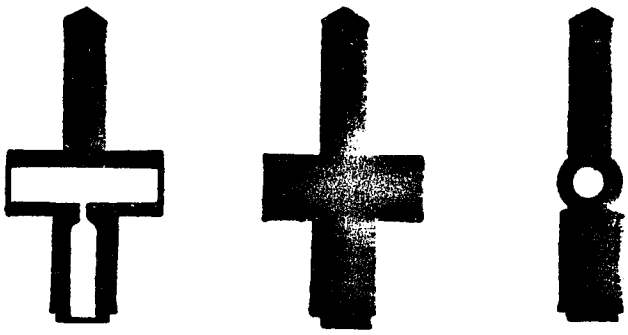


FIGURE 8: Resistance Heated Carbon Element

transformer. This allowed very high currents at relatively low voltages. Because of the low resistance of the carbon electrode, high currents were required to attain high atomizer temperatures. The optical system of the A.A. consisted of a sealed hollow cathode lamp (Pb) which was later replaced with a demountable hollow cathode lamp, a chopper, 2 focusing lenses, and a monochrometer. This was connected to an amplifier and a recorder.

3. The Gas Chromatograph-Atomic Absorption Interface

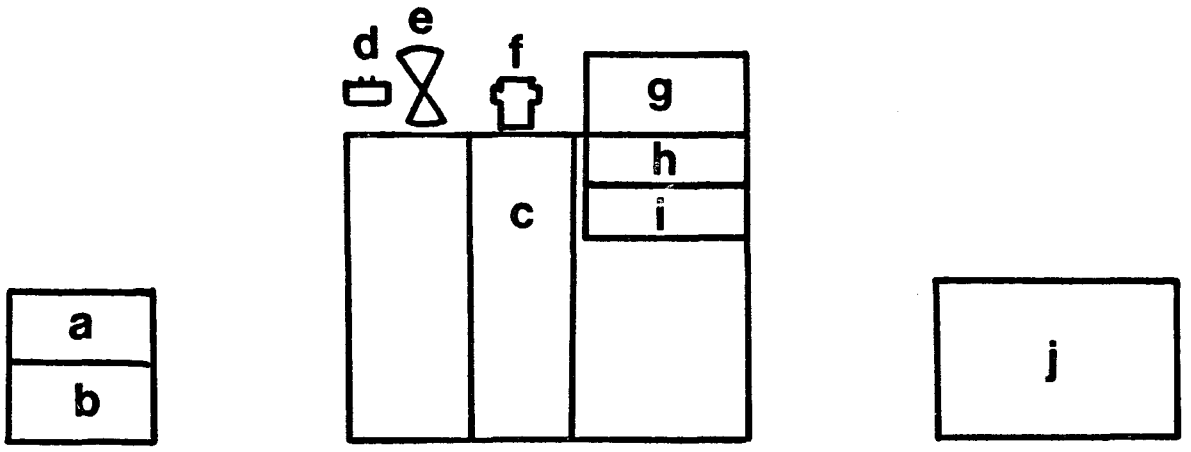
An eighth-inch steel plate was placed on top of the G.C. to act as an optical table for the magnetically mounted optical components of the A.A. A 1/2 inch diameter hole was drilled through the plate to allow the transfer line and its heater passage. The G.C. was directly interfaced to the lower electrode with a stainless steel transfer line. The transfer line was sealed to the electrode by means of a teflon ferrule which also served to electrically isolate it from the electrode. A chromel-alumel thermocouple pyrometer was used to monitor the transfer line temperature. The stainless steel transfer line was later replaced with pyrex capillary tubing.

4. Equipment (Figure 9)

a. Standard components

1) Gas Chromatograph - Microtek Model G.C.-2000-R

2) Monochrometer - Varian Techtron



a. HCL Power Supply
b. HCL Presure Gauge
c. G.C. Oven
d. Hollow Cathode Lamp
e. Chopper
f. Atomizer Detector
g. Monochrometer
h. High Voltage Power Supply for P.M. Tube
i. Amplifier
j. Recorder

FIGURE 9: G.C.-A.A. Equipment

3) Amplifier - Heathkit Photometric Readout Model EU-703-31

4) Recorder - Sargent Model SR with variable range attachment

5) High Voltage Power Supply - Hewlett-Packard Model 6515A

6) Photomultiplier tube - Hamamatsu Corp. R-106

7) Hollow Cathode Lamp - Jarrell-Ash Sealed Hollow Cathode (Pb) and Barnes Engineering Co. - Glomax demountable hollow cathode

8) Stepdown Transformer - Signal Transformer Co. Model 6-260 (6 volts - 250 amps max.)

9) Variable Autotransformer - Superior Electric Co. Powerstat (2KVA)

10) Microliter Syringe - Hamilton 0-10 microliter

B. DETERMINATION OF LEAD ALKYLS IN GASOLINE BY GAS CHROMATOGRAPHY-ATOMIC ABSORPTION

1. Introduction

The determination of lead alkyls in gasoline was a necessary step to demonstrate the potential of G.C.-A.A. It was part of a separate endeavor to characterize the chemical form of molecular lead in the atmosphere. Gas chromatographic techniques utilizing an electron capture detector to determine lead alkyls are well established.[27]

Because of similar retention times, the "scavengers" (ethylene chloride and ethylene bromide) in gasoline completely obscured the dimethyl diethyl lead peak on E.C.D. unless special precautions were taken to remove them. Thus pretreatment of the sample was required.

Care must be taken to avoid decomposition of the sample in the G.C. column. This phase of gas chromatography has

been well documented and need not be repeated here.

Column bleed is often a problem in gas chromatography. The column packing material used in this study was tricresyl phosphate on Chromosorb W, stable to 125°C. The detection limit of an E.C.D. is 10^{-14} grams (1 µL sample volume) for organophosphates. With the normal column operating temperature of 105-115°C some column bleed was induced. This causes much interference for an E.C.D. The A.A. detector totally decomposed the tricresyl phosphate and, being more selective, was completely insensitive to it.

The relative retention times of the five lead alkyls in gasoline were determined. The detector response for the lead in lead alkyls was determined by running dilutions of a 374 µg/mL tetramethyl lead solution in n-heptane.

Leaded gasolines were then analyzed and lead was determined as lead alkyls. The precision of analysis was measured and operating characteristics were noted.

2. Experimental Parameters

   a. Gas Chromatograph Parameters

      1) Column - 1/8 inch diameter stainless steel, 30 inches long, packed with 20% tricresyl phosphate on Chromosorb W (Teklab, Inc.)

      2) Carrier gas - Argon (150 cc/min)

      3) Column temperature - 95°C

      4) Injection Port temperature - 100°C

      5) Transfer line temperature - 105°C

b. Atomic Absorption Parameters

1) Lamp current - 8 ma.

2) High voltage to photomultiplier tube - 620 VDC

3) Slit width - 150 microns

4) Analytical wavelength - 283.3 nm

5) Atomizer temperature - 2000°C

c. Chemicals

1) n-heptane - Eastman Chemicals

2) Tetramethyl lead solution (374 µg/mL) - Ethyl Corp.

3) Gasoline samples - area station owners

4) Mixed lead alkyl solution - Ethyl Corp.

3. Experimental Procedure

The relative retention times of the lead alkyls on the gas chromatographic column were determined by injecting a one microliter sample of a mixed lead alkyl solution known to contain the five lead alkyl compounds present in leaded gasolines (i.e., tetramethyl lead [TML]; trimethylethyl lead [TMEL]; dimethyldiethyl lead [DMDEL]; methyltriethyl lead [MTEL]; and tetraethyl lead [TEL]).

After the relative retention times were determined, samples of various brands and blends of gasolines were analyzed for lead alkyl content (Table 1, Figures 10-13). A variation in lead alkyl content was noted from station to station for the same grade and manufacturer (Table 2). The system was calibrated using dilutions of a 374 µg/mL

Table 1 - Lead Alkyl Distributions in Gasoline by Manufacturer and Grade

MANUFACTURER	Texaco				Mobile			
GRADE	Premium		Regular		Premium		Regular	
Pb ALKYL	ppm	%	ppm	%	ppm	%	ppm	%
TML	13	4	3	2	26	9	23	10
TMEL	54	15	15	7	101	37	71	31
DMDEL	21	33	60	28	103	37	90	39
MTEL	126	34	92	43	37	13	38	17
TEL	57	15	43	20	9	3	8	3

MANUFACTURER	Shell				Exxon			
GRADE	Premium		Regular		Premium		Regular	
Pb ALKYL	ppm	%	ppm	%	ppm	%	ppm	%
TML	18	7	24	7	20	10	28	10
TMEL	90	33	110	34	61	32	86	32
DMDEL	123	45	122	37	72	37	111	41
MTEL	38	14	64	19	33	17	33	12
TEL	7	3	8	2	7	4	10	4

% = percent of total lead alkyl content

TML = tetramethyl lead

TMEL = trimethylethyl lead

DMDEL = dimethyldiethyl lead

MTEL = methyltriethyl lead

TEL = tetraethyl lead

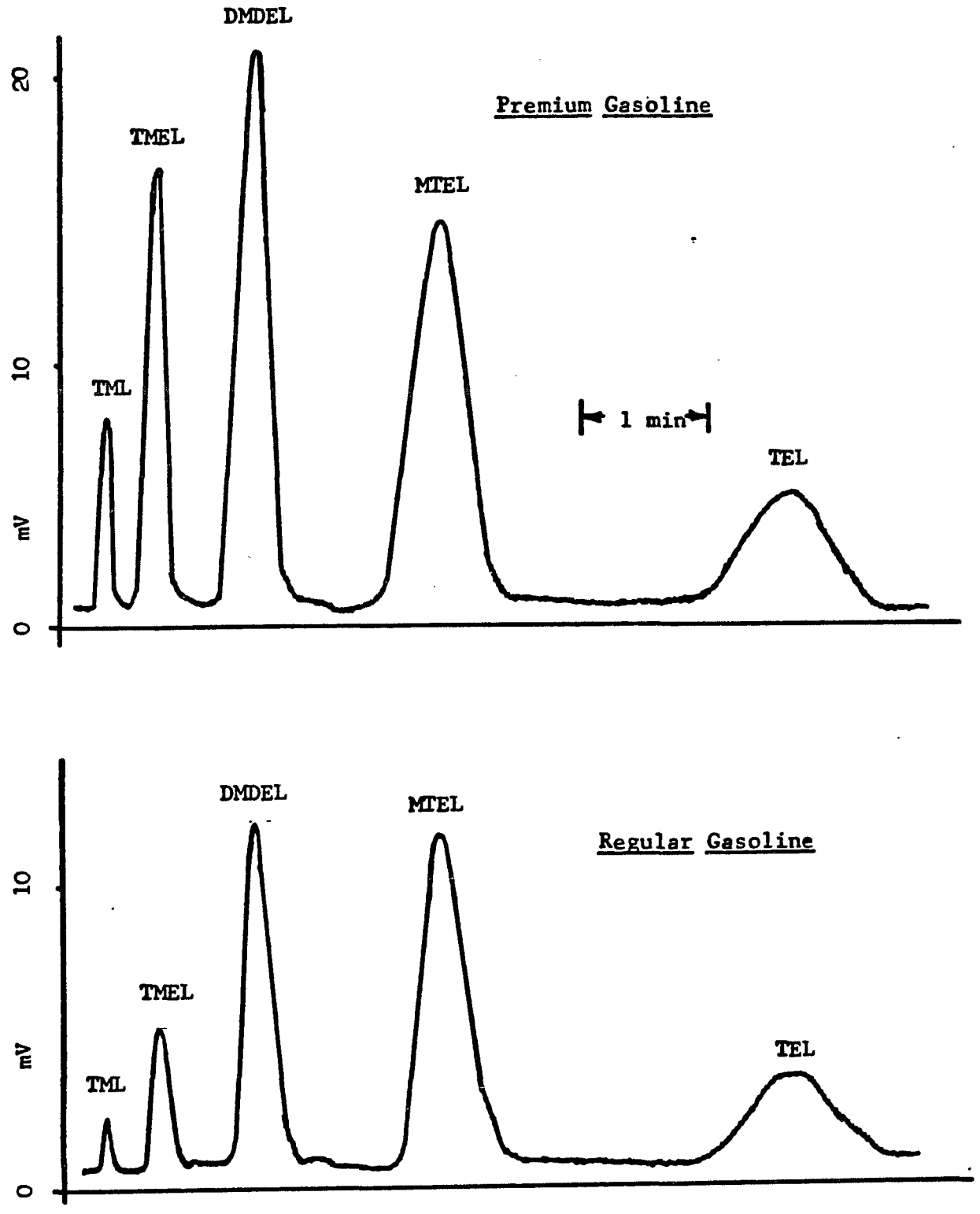


FIGURE 10- Gas chromatographic traces for gasolines, Texaco.

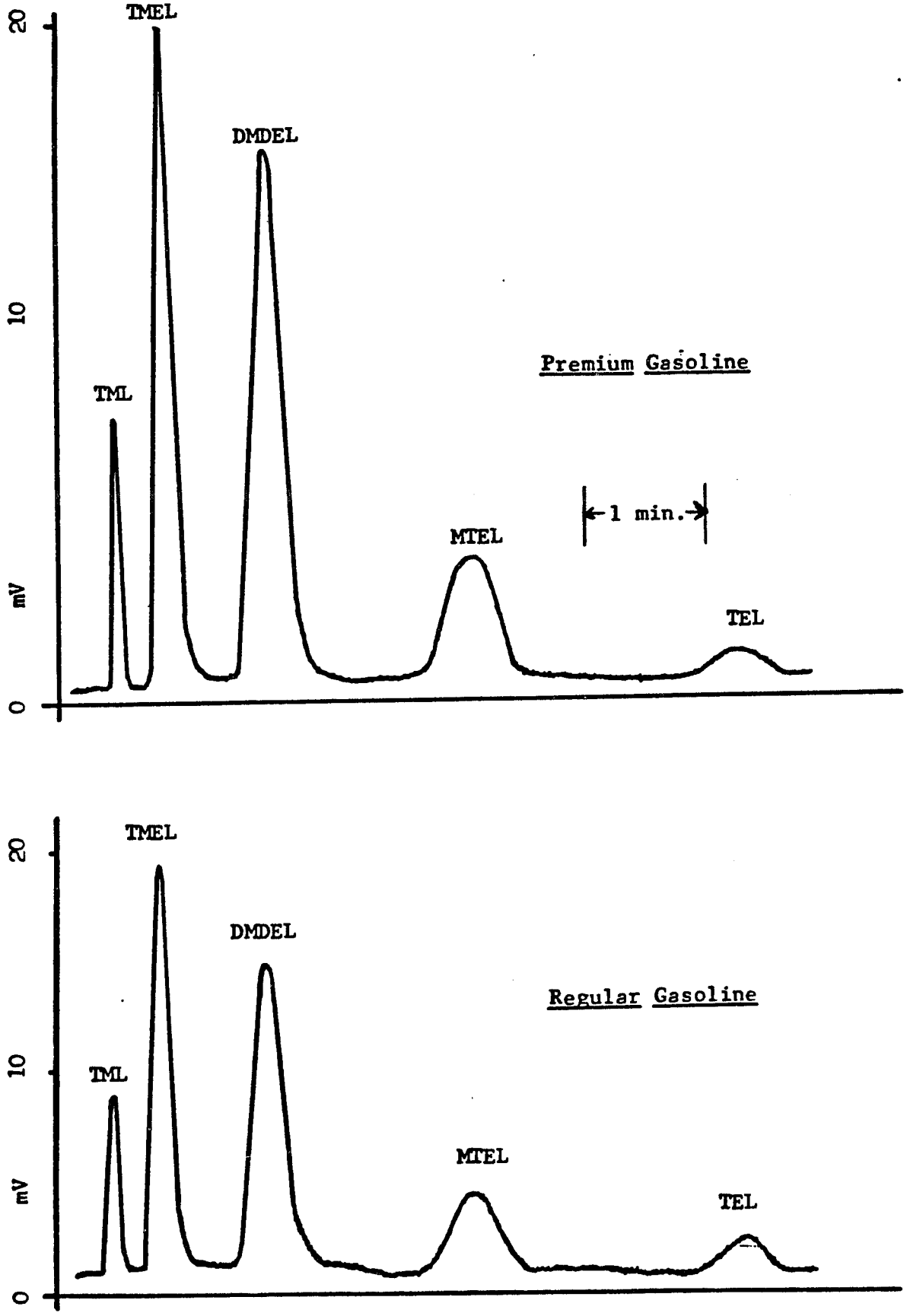


FIGURE 11- Gas chromatographic traces for gasolines, Mobile.

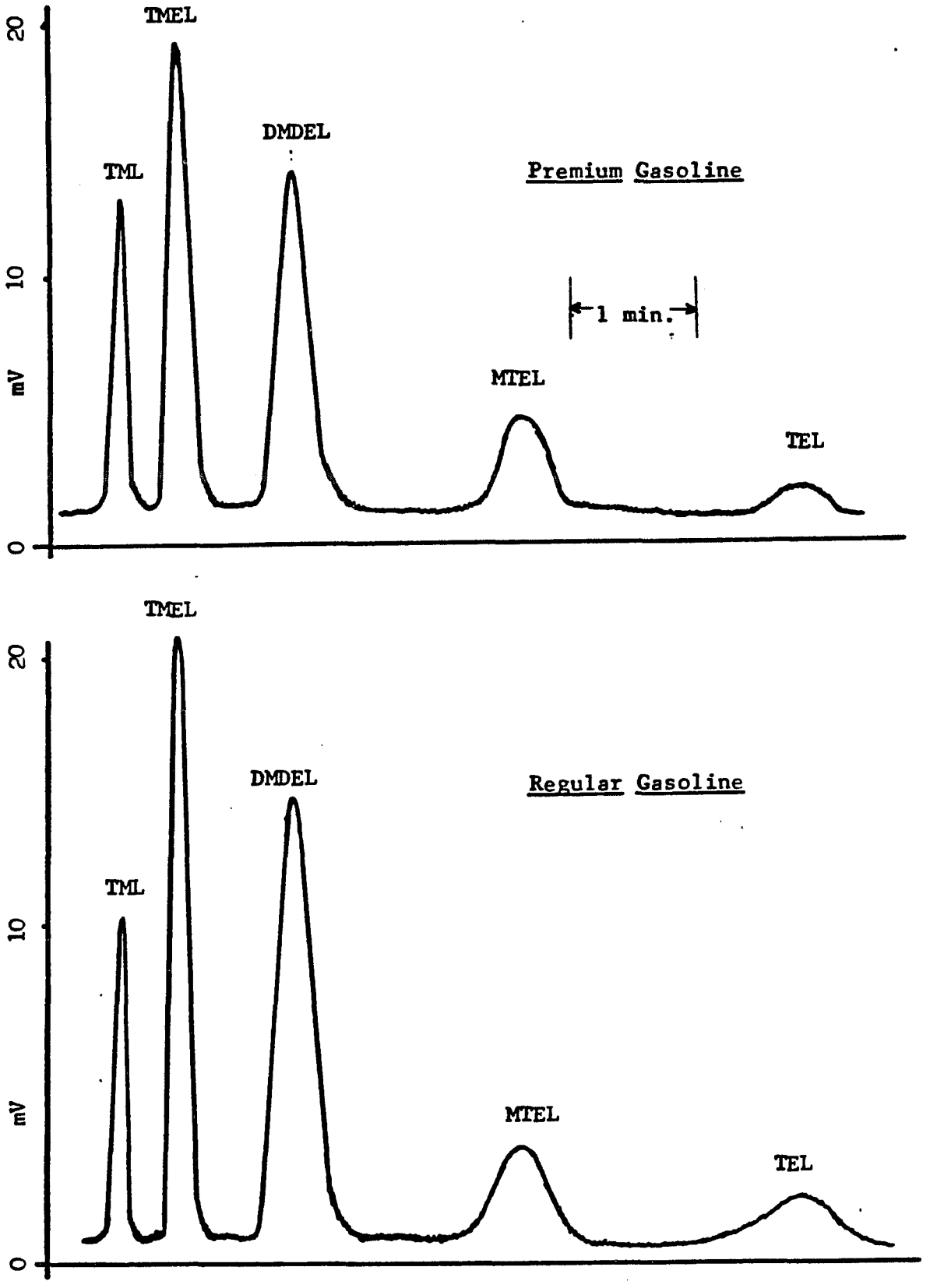


Figure 12- Gas chromatographic traces for gasolines, Shell.

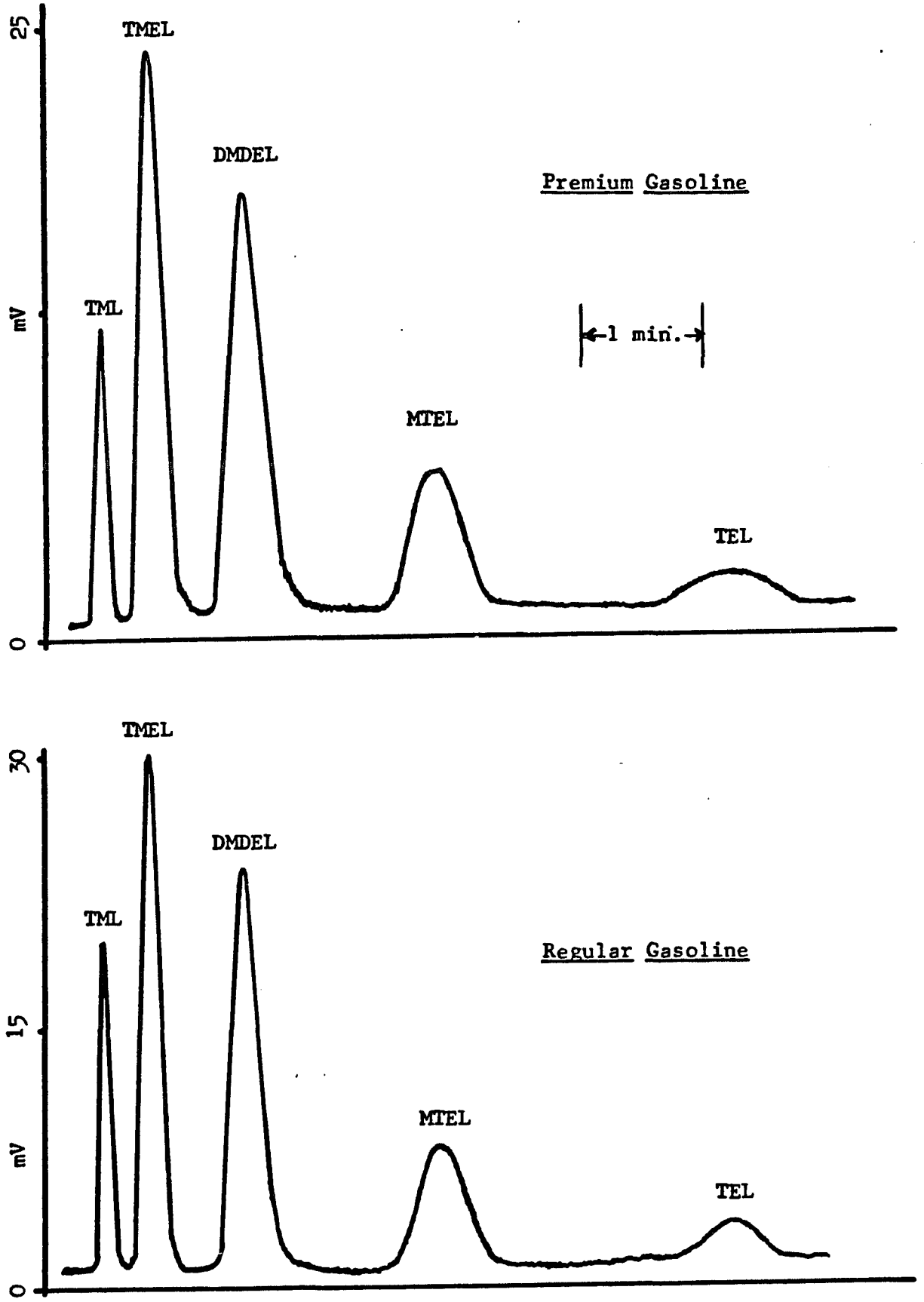


FIGURE 13-Gas chromatographic traces for gasolines, Exxon.

Table 2 - Variation in Lead Alkyls from Station to Station for Same Grade and Manufacturer

Station No.	1		2		3		4	
Pb. Alkyl	ppm	%	ppm	%	ppm	%	ppm	%
TML	9	1	21	2	18	1	19	2
TMEL	57	6	94	9	115	8	83	7
DMDEL	248	26	245	23	334	24	288	25
MTEL	442	46	500	46	580	41	476	42
TEL	204	21	216	20	368	26	276	24

TML solution in n-heptane. The precision of analysis was determined by making 10 injections (1 μL sample volume) of TML.

Once the calibration was complete, the lead hollow cathode lamp was replaced with a deuterium lamp and the entire group of samples and standards were re-run to determine any molecular or background absorption.

The operating characteristics were noted and several modifications were made to the instrument to improve sensitivity. After the modifications were made, a second set of gasoline samples were analyzed (Figures 14a-18c) for lead content as lead alkyls. Molecular background absorption was corrected by re-running the entire group of samples after replacing the lead hollow cathode lamp with a deuterium lamp.

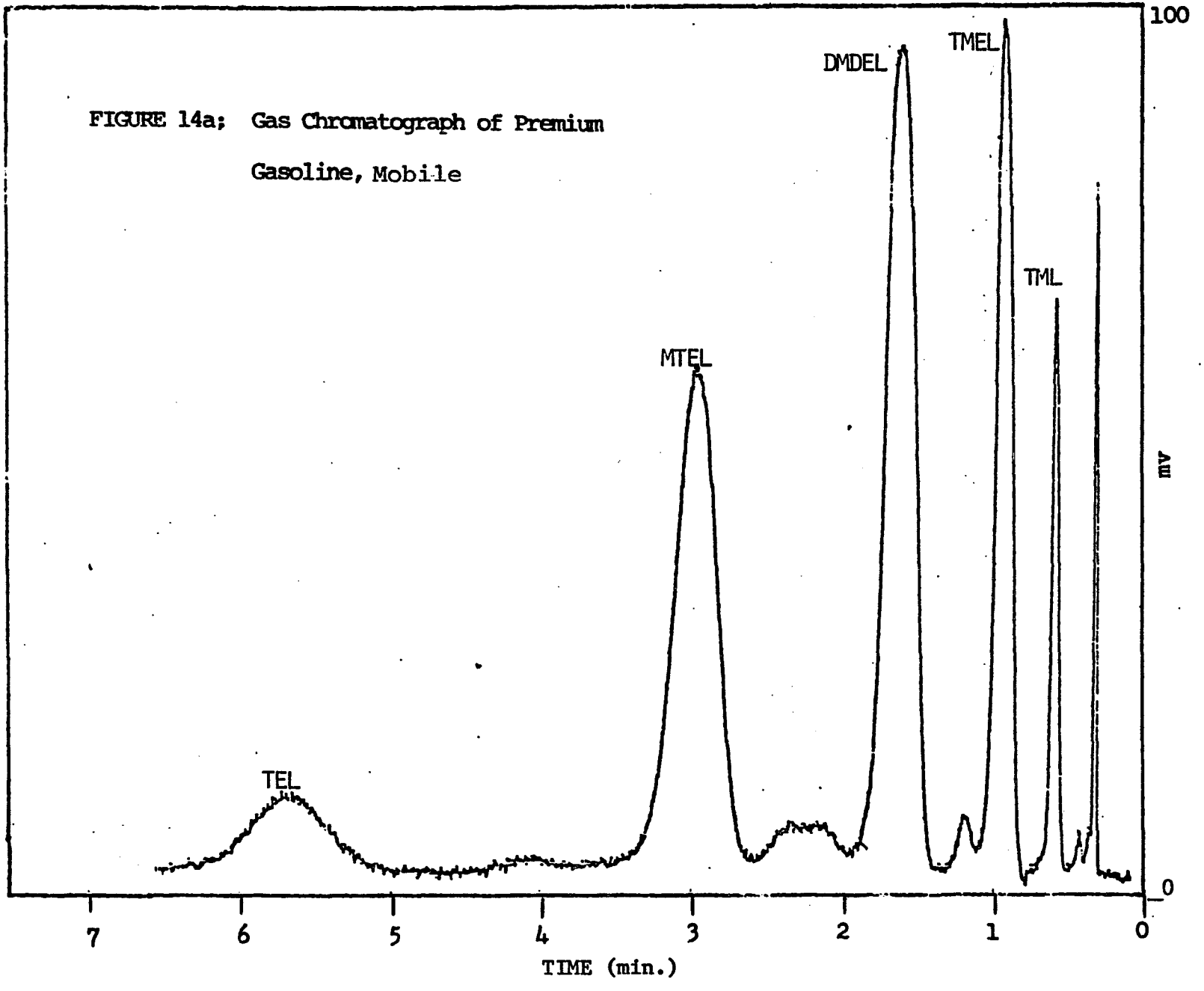
4. Results and Discussion

a. Practical Applications of the Gas Chromatography-Atomic Absorption System

The new atomic absorption detector for gas chromatography exhibited the excellent specificity of atomic absorption while retaining the sensitivity of electrothermally heated carbon atomizers.

The five lead alkyls in gasoline were separated on the G.C.-A.A. and their relative retention times were established. The lead alkyl content of various blends of gasoline from several manufacturers was determined (Table 1, Figures 10-13). A basic pattern or "fingerprint" existed

FIGURE 14a; Gas Chromatograph of Premium Gasoline, Mobile



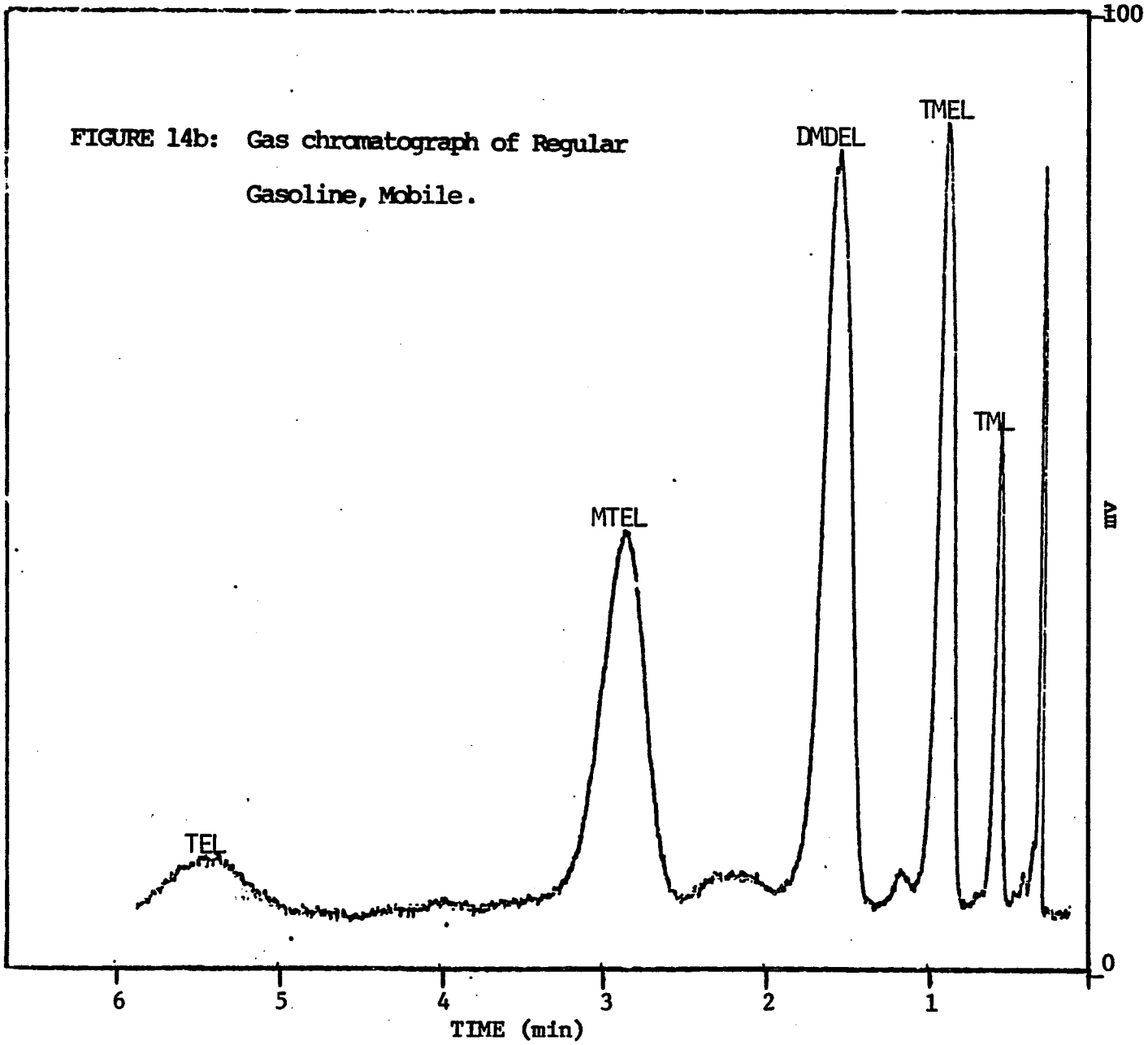


FIGURE 14b: Gas chromatograph of Regular Gasoline, Mobile.

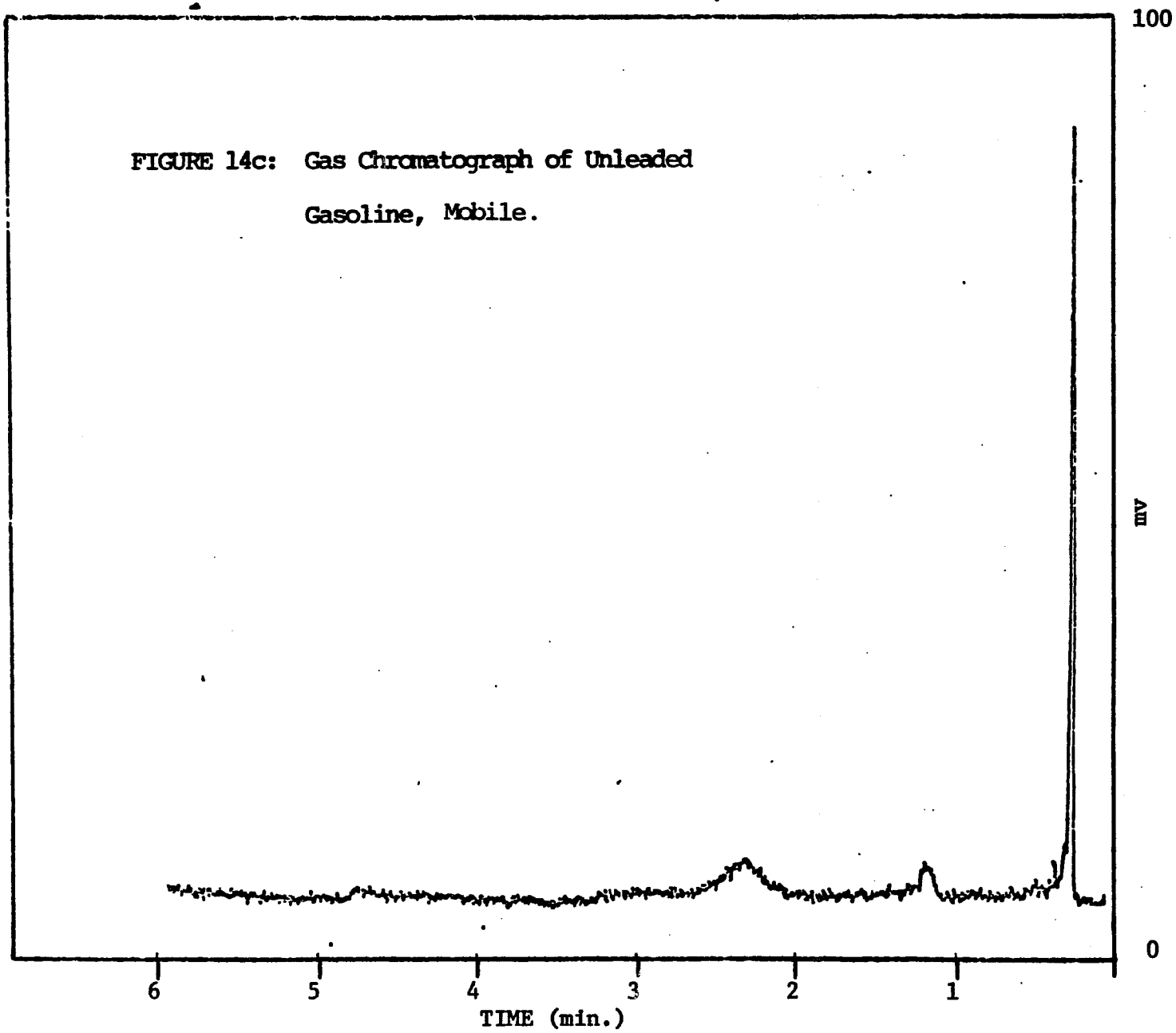


FIGURE 14c: Gas Chromatograph of Unleaded Gasoline, Mobile.

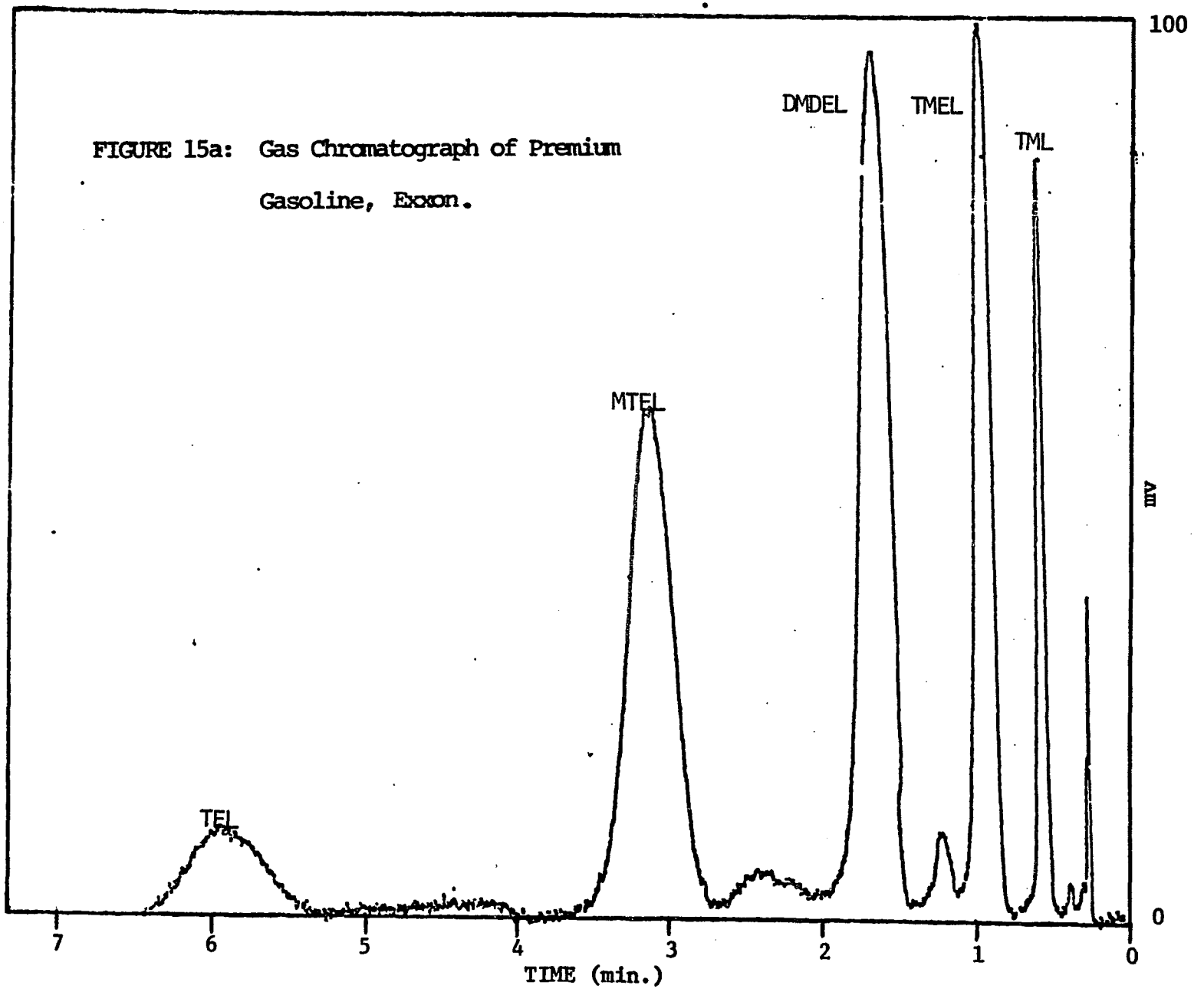


FIGURE 15a: Gas Chromatograph of Premium Gasoline, Exxon.

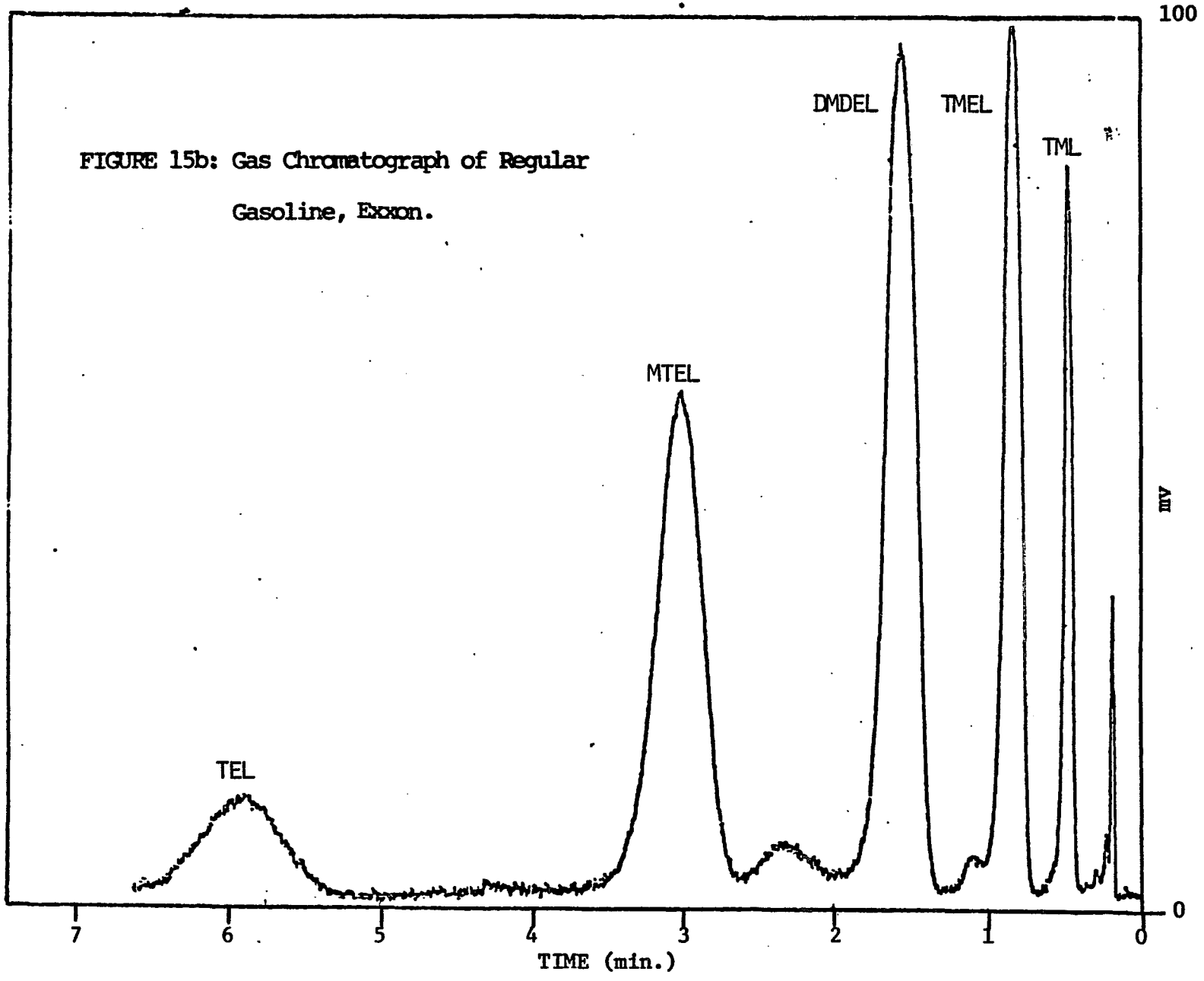


FIGURE 15b: Gas Chromatograph of Regular Gasoline, Exxon.

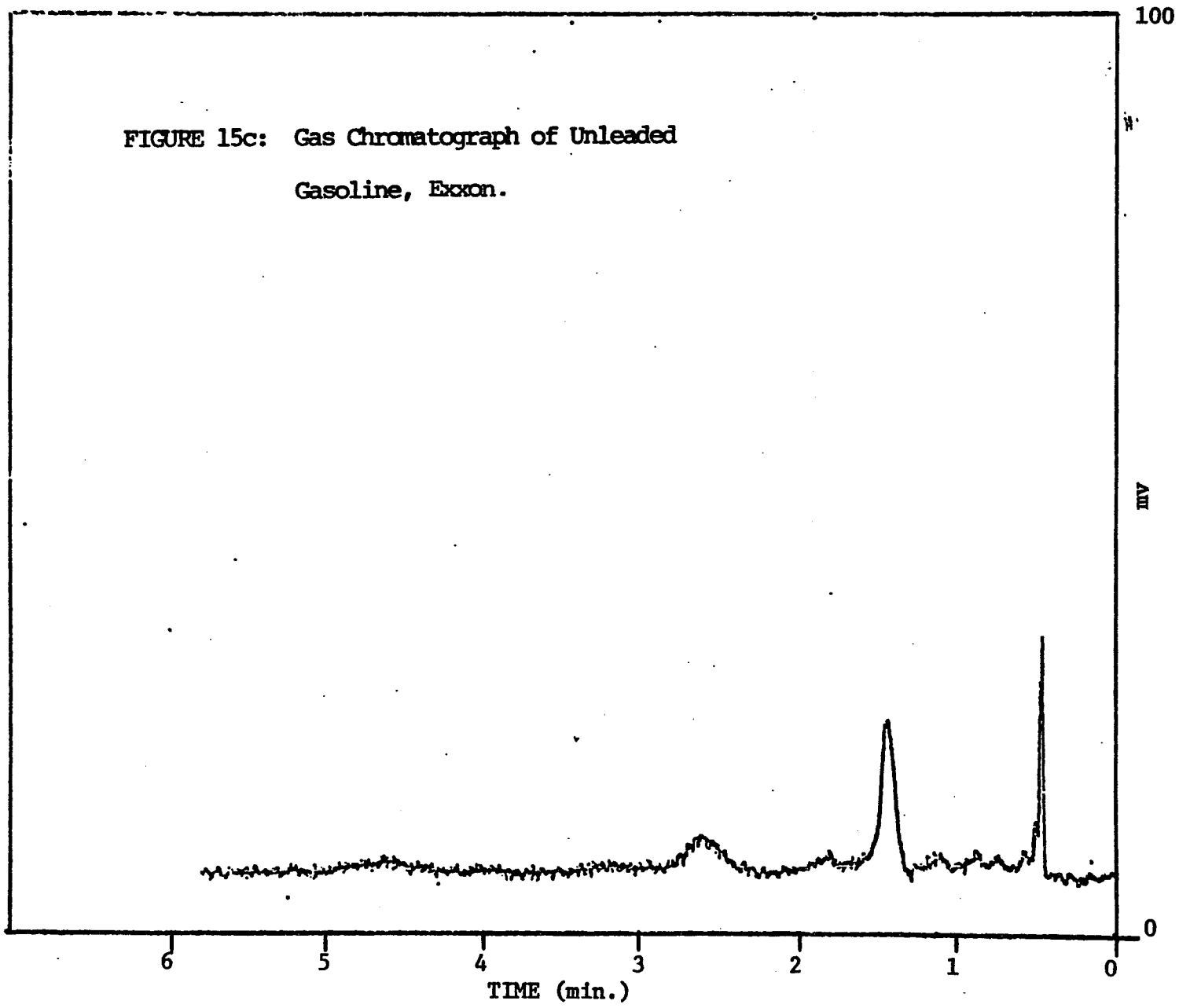


FIGURE 15c: Gas Chromatograph of Unleaded Gasoline, Exxon.

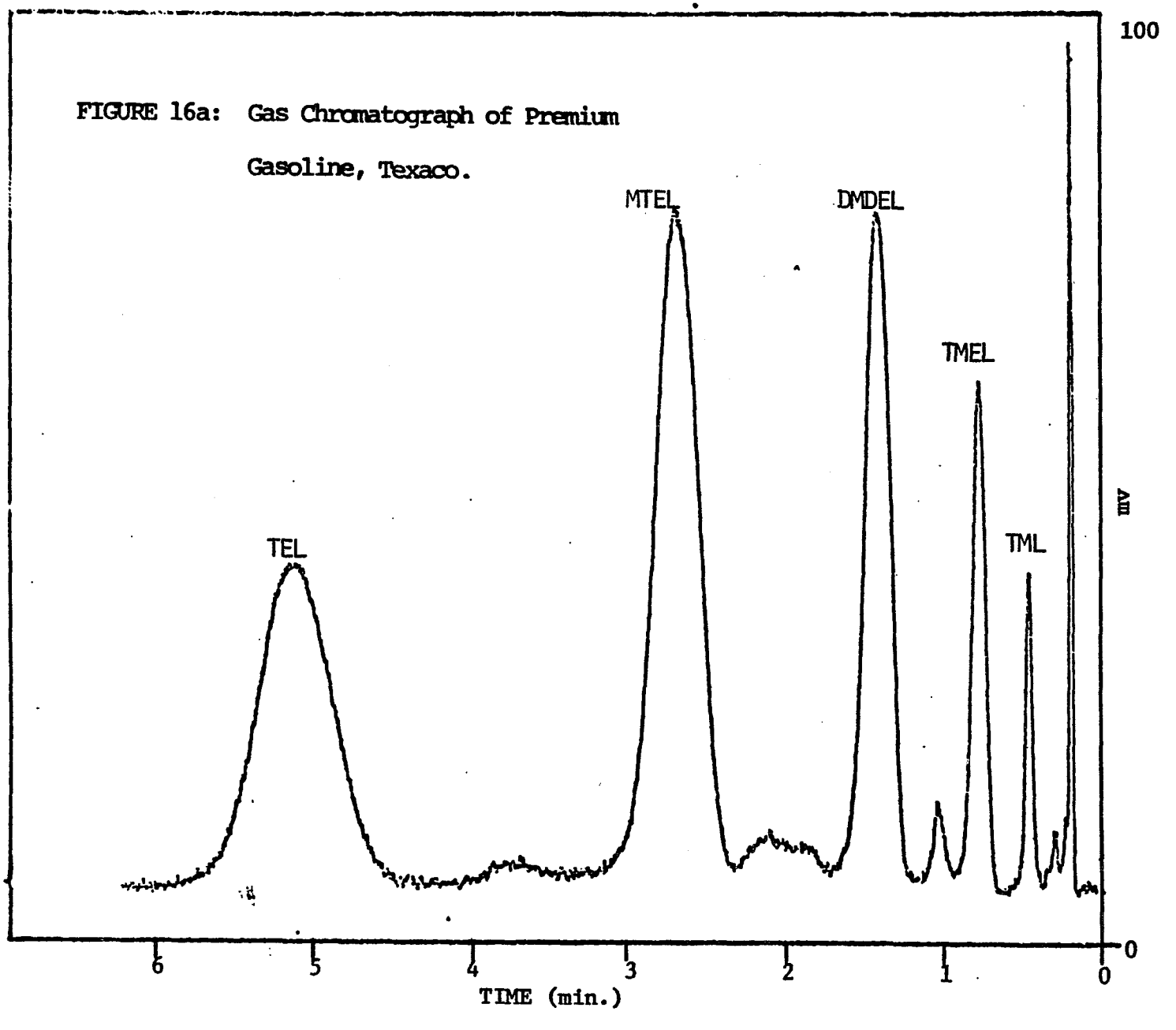
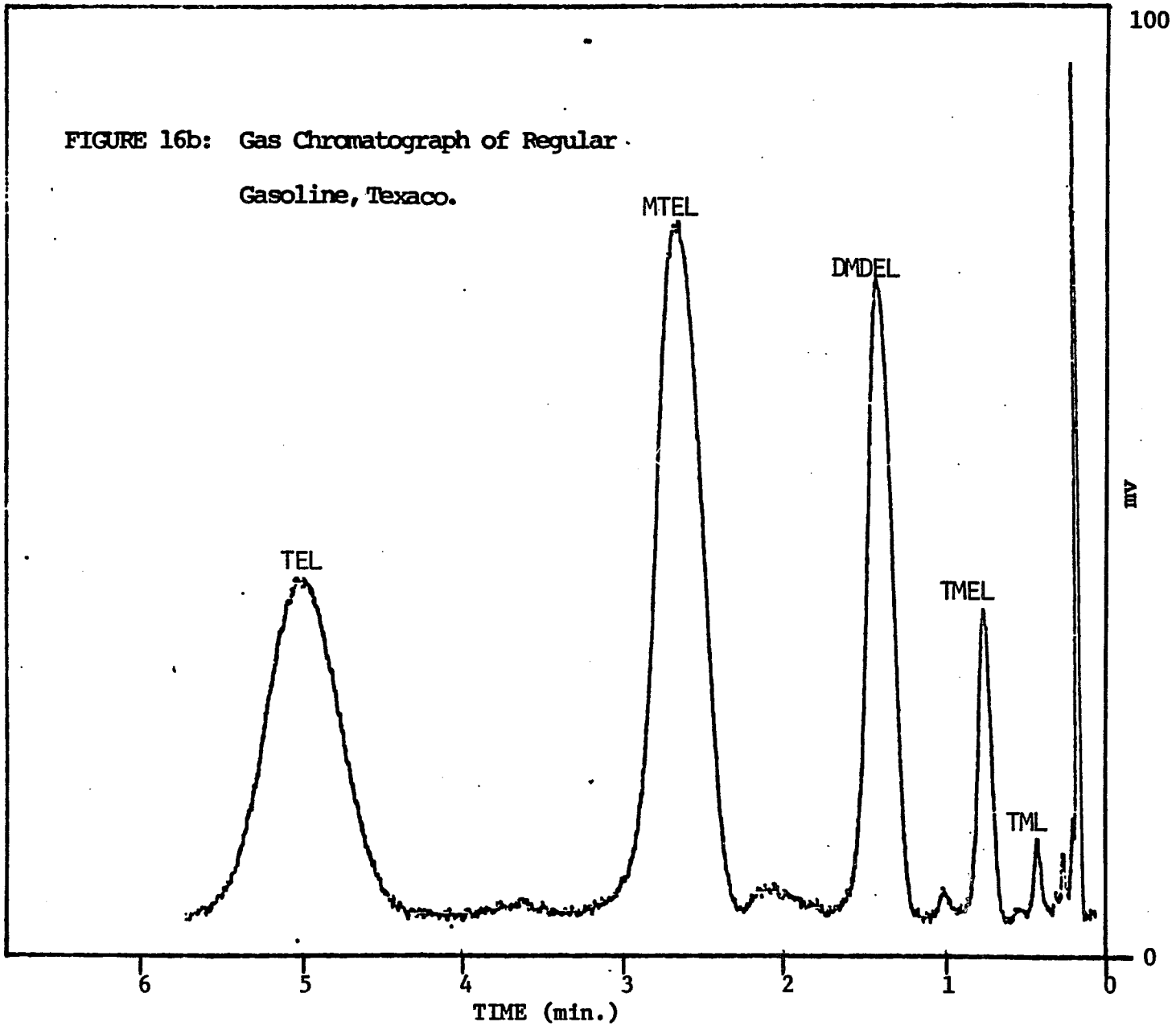


FIGURE 16a: Gas Chromatograph of Premium Gasoline, Texaco.

FIGURE 16b: Gas Chromatograph of Regular Gasoline, Texaco.



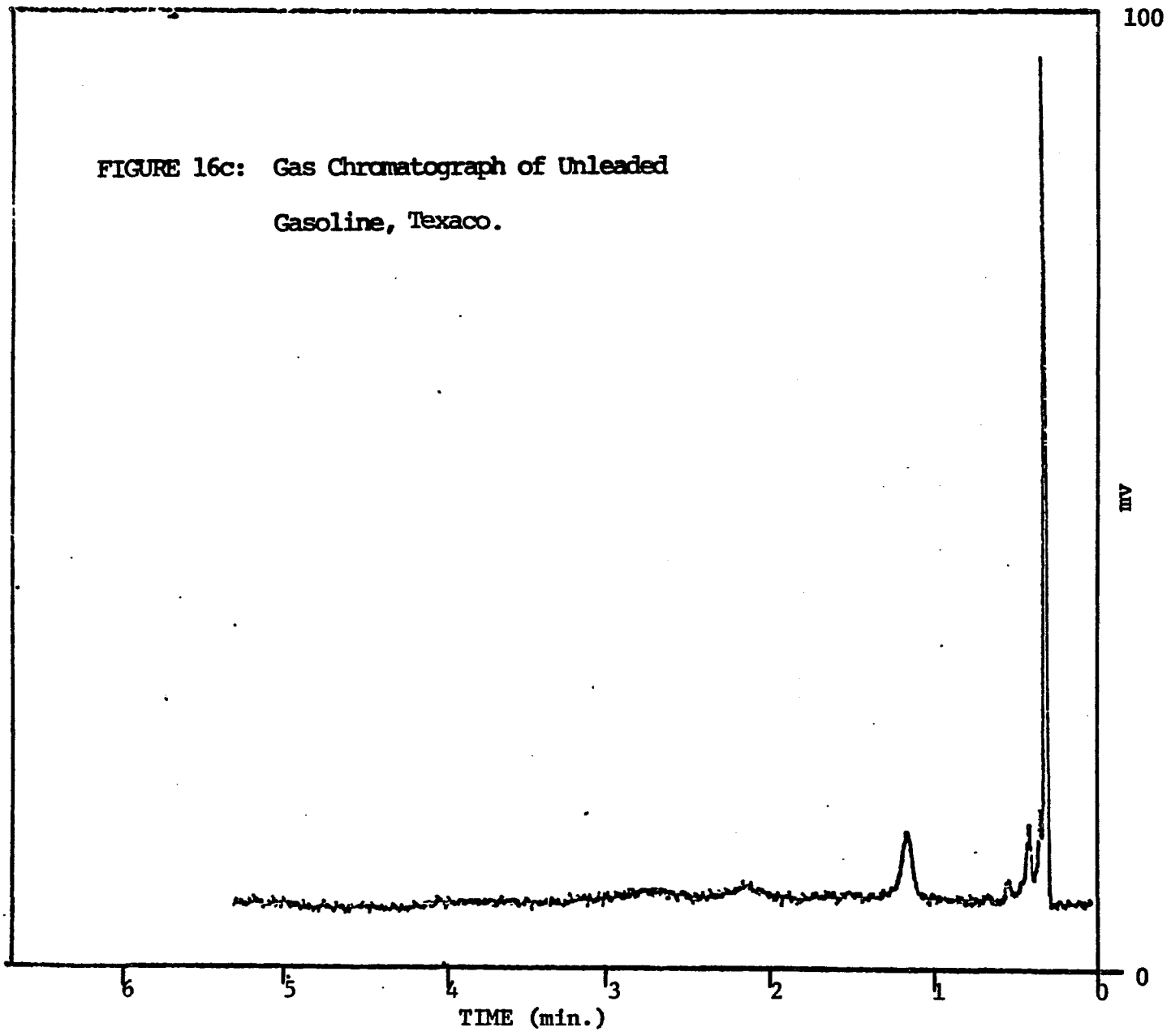


FIGURE 16c: Gas Chromatograph of Unleaded Gasoline, Texaco.

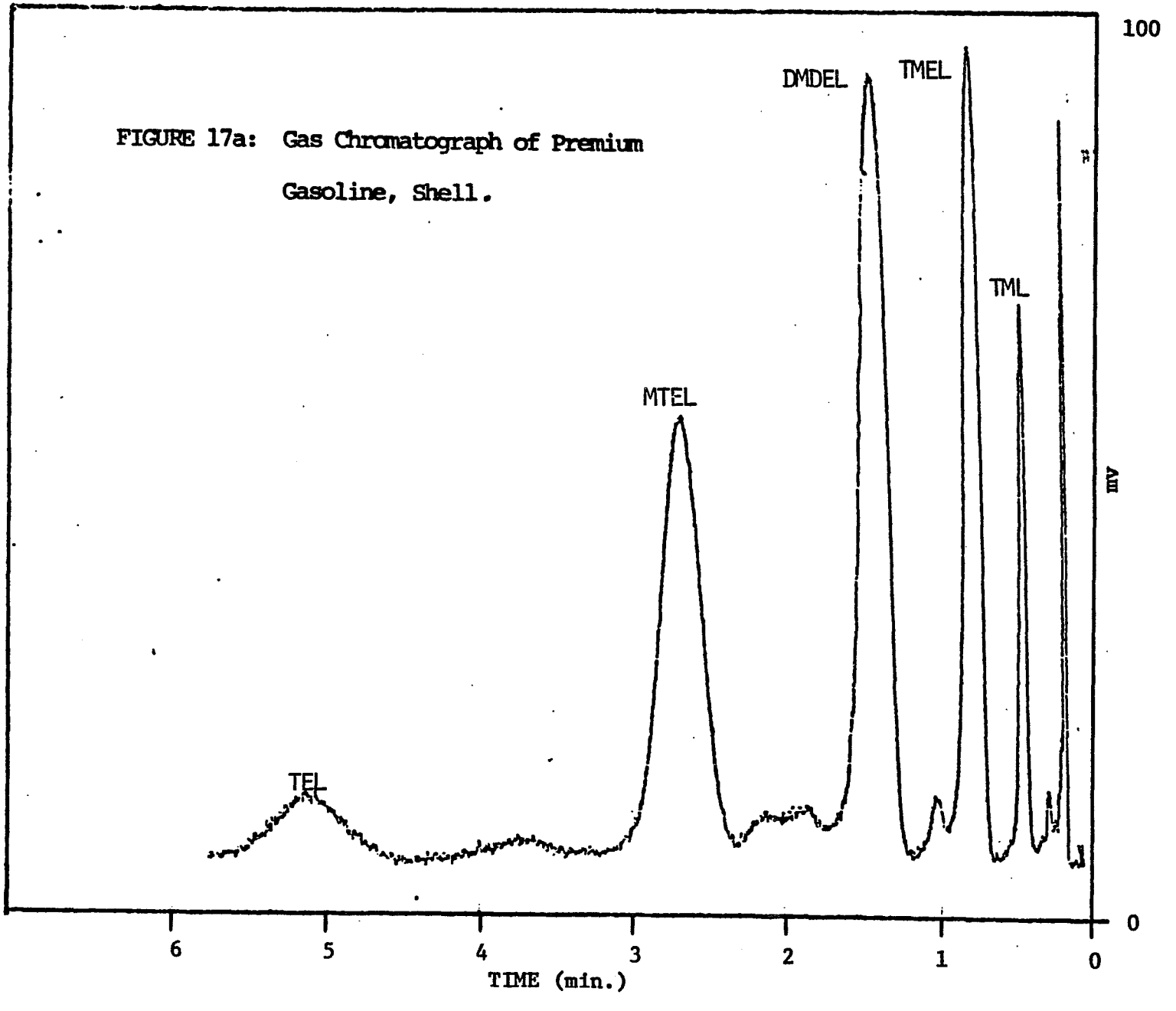


FIGURE 17a: Gas Chromatograph of Premium Gasoline, Shell.

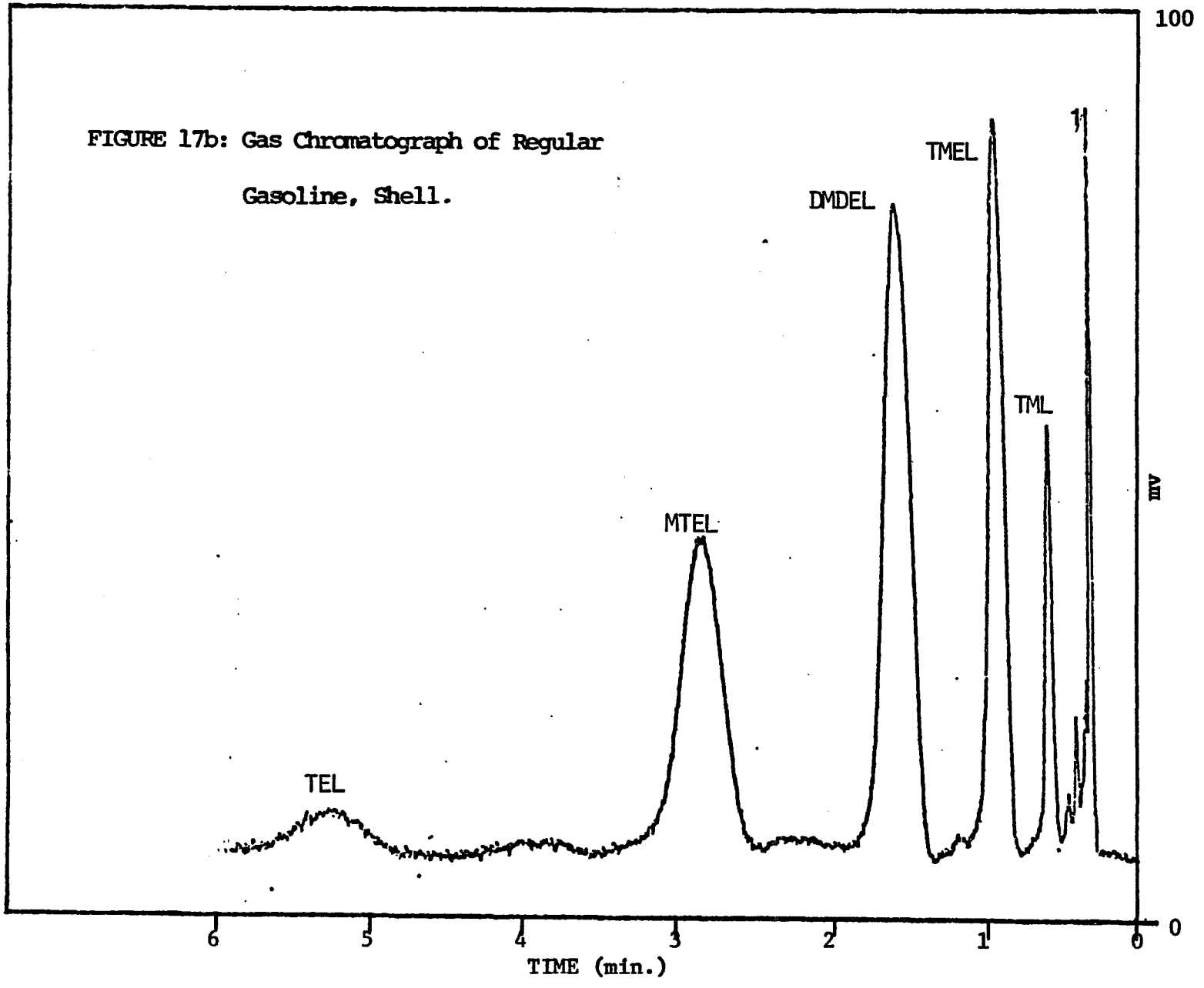


FIGURE 17b: Gas Chromatograph of Regular Gasoline, Shell.

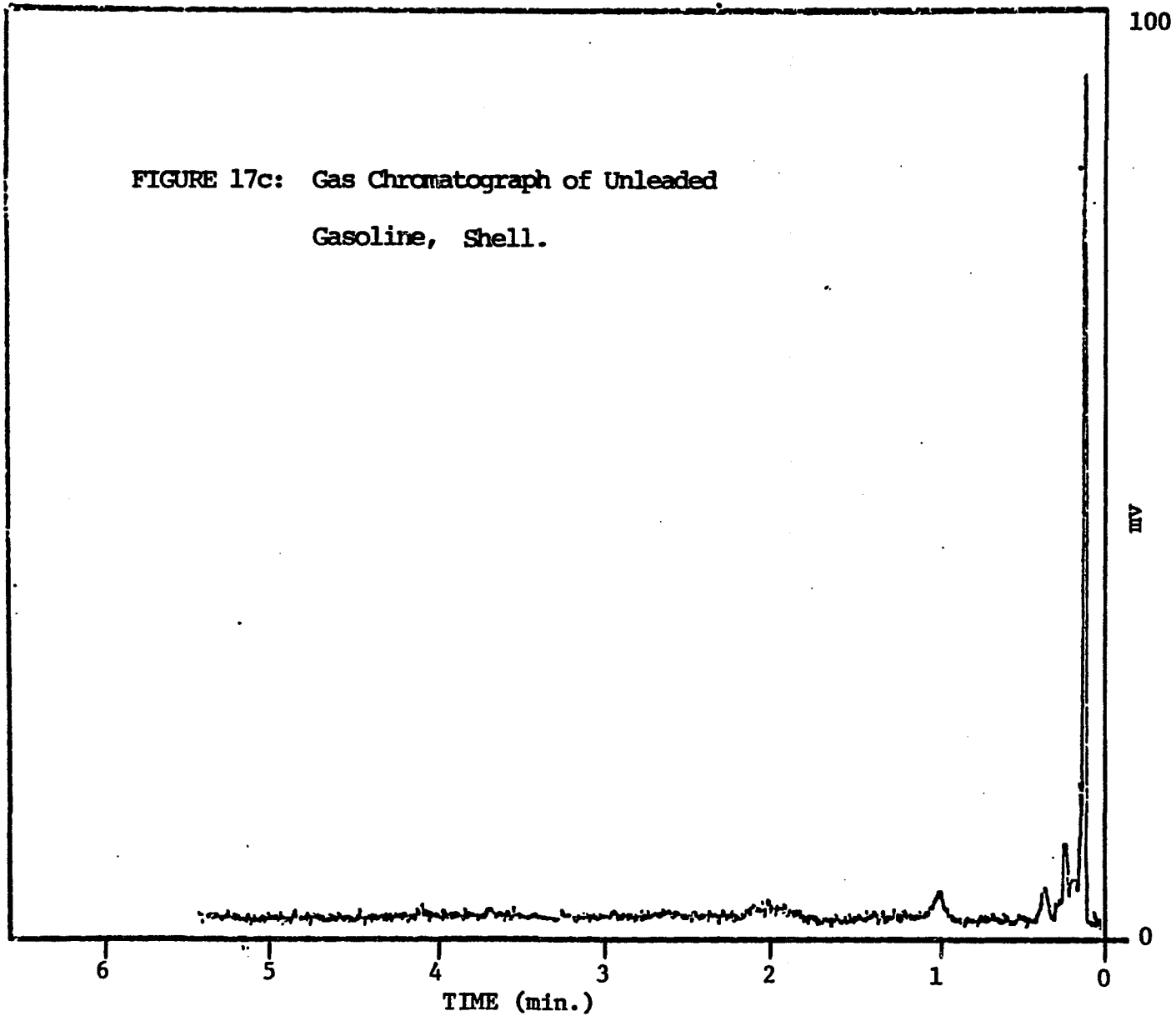


FIGURE 17c: Gas Chromatograph of Unleaded Gasoline, Shell.

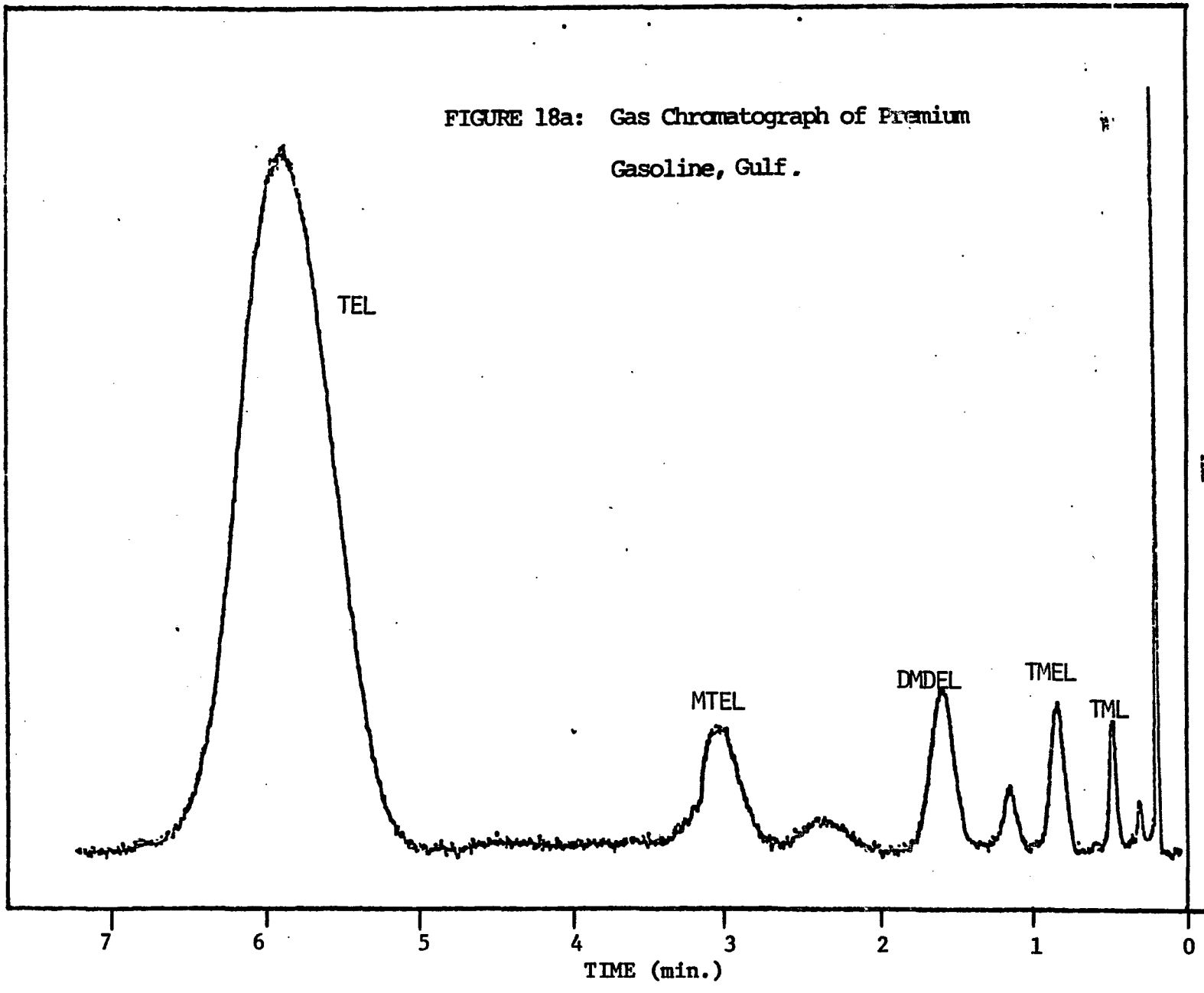


FIGURE 18a: Gas Chromatograph of Premium Gasoline, Gulf.

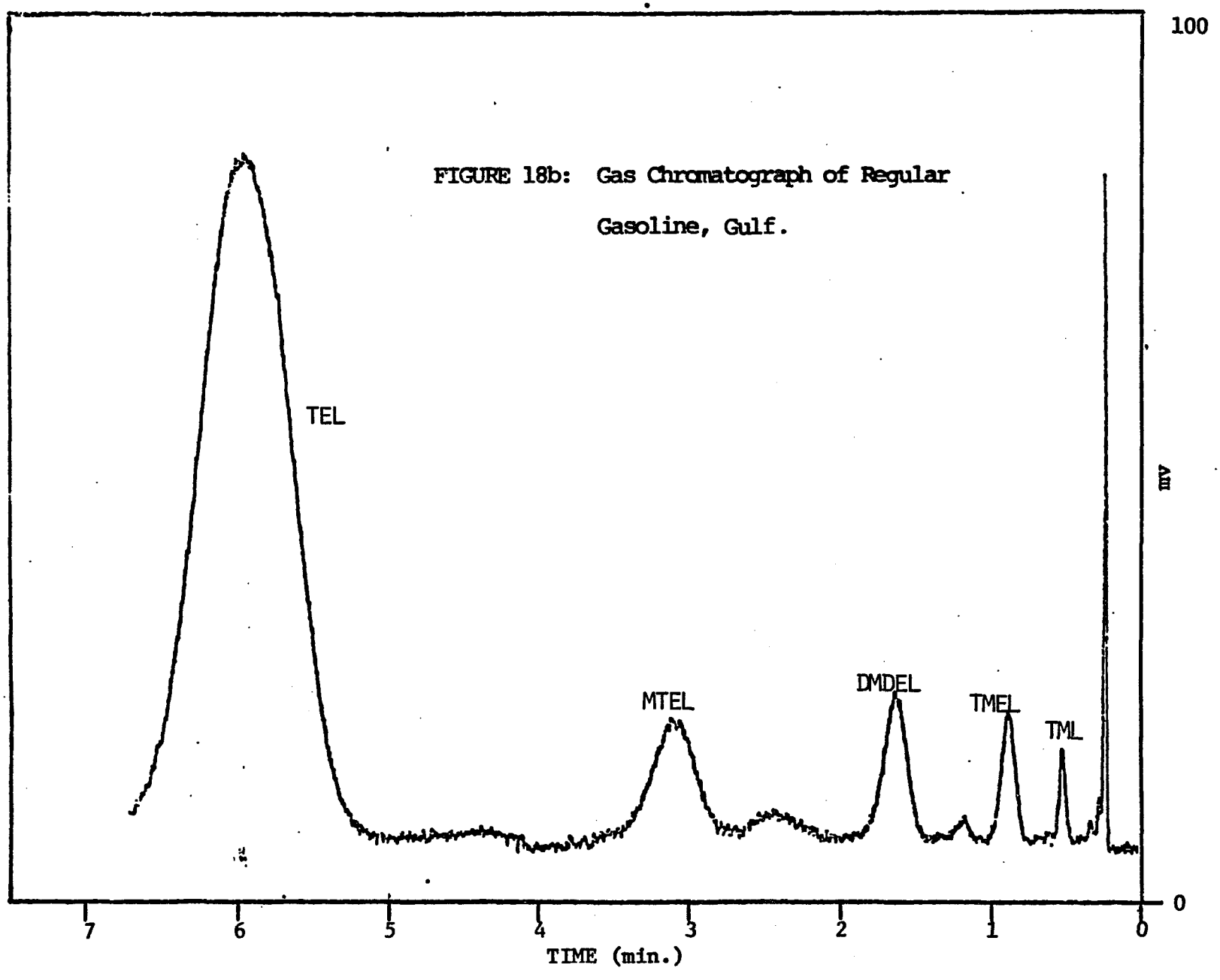


FIGURE 18b: Gas Chromatograph of Regular Gasoline, Gulf.

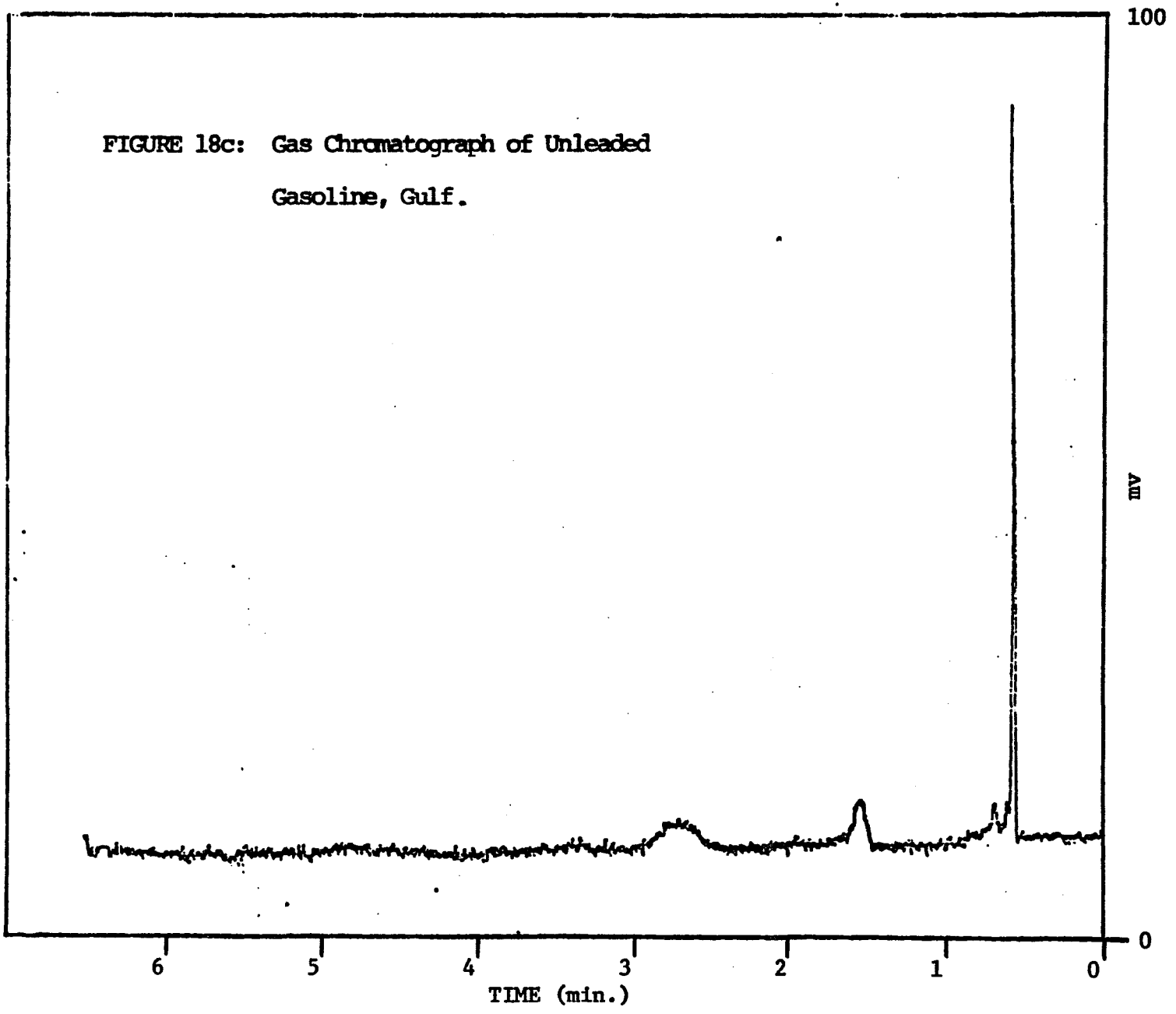


FIGURE 18c: Gas Chromatograph of Unleaded Gasoline, Gulf.

for each manufacturer's blends based on the variations of concentration of the five lead alkyls in leaded gasoline. The lead alkyl content of a grade of gasoline for a given manufacturer tended to vary from station to station (Table 2). The basic pattern, however, was still evident.

b. Precision of Analysis

Precision of analysis was determined by making 10 injections (1 μL sample volume) of TML. The relative standard deviation was 2% (Table 3). Larger variations were unavoidable in real samples. TML peaks were sharp and symmetrical whereas the larger lead alkyls were much broader. Areas were measured by triangulation.

Increased precision can be achieved by increasing sample size to a more reproducible volume. Error in measurement can be reduced by using a more accurate method of determining chromatograph areas (e.g., planimeter, mechanical integrator, etc.).

c. Molecular Background Absorption

A deuterium lamp was used to measure background absorption. Repeated injections of gasoline, n-heptane and standards indicated negligible background absorption interference from the solvents and none from the decomposition of the lead alkyl compounds.

If complete decomposition of a sample occurs before the sample reaches the atomic absorption light path, molecular absorption can be reduced.[73] Invariably, H_2 is formed in

Table 3 - Precision of Injection of TML Solution

Injection No.	Area	Injection No.	Area
1	127	6	126
2	122	7	124
3	122	8	123
4	125	9	125
5	122	10	124

Average area - 124

percent relative deviation - 2%

the atomization process and absorbs radiation at wavelengths less than 230.0 nm.[64]

Molecular background from gasoline was negligible. This was probably due to the excellent combustion properties of gasoline.

d. Operating Characteristics

The most important operating characteristic of the atomizer was the lifetime of the resistance heated carbon element. The average lifetime of the carbon element was 24 continuous hours of operation. Decomposition of the carbon element appeared to occur from the outside, not the inside. This was presumed to be a reaction between the heated carbon and atomospheric oxygen that leaked into the atomizer. The carbon element was easily replaced every few days.

There were no mechanical difficulties with construction or operation of the atomizer. High temperatures could be reached with relatively low electrical power output.

Temperatures less than 2000°C were normally used. Lead alkyls tended to decompose completely at these lower temperatures. A temperature versus atomization efficiency study indicated no increase in atomization efficiency for lead alkyls at temperatures greater than 1800°C.

e. Sensitivity Improvements

The sensitivity of the instrument was 1.5 x 10^{-9} g per 1 µL sample volume. This was approximately 30 times greater than a similar A.A. flame detector for G.C.

It was felt that with minor modifications, the

sensitivity of the G.C.-A.A. could be improved without altering the atomizer. These modifications included replacing the stainless steel transfer line with glass, finding a replacement material for the stainless steel column, and replacing the sealed hollow cathode lamp with a demountable hollow cathode lamp.

The demountable hollow cathode lamp was more intense and stable than the sealed lamp. The more intense light source allowed the use of a lower photomultiplier (P.M.) tube voltage. The lower P.M. tube voltage decreased the dark current noise.[64]

The stainless steel column was replaced with pyrex tubing. It was later decided to replace the pyrex tubing with teflon tubing. There was approximately a 3 fold increase in sensitivity with the same size teflon column rather than pyrex. It is possible that there were many active sites (SiO_2) on the pyrex that degraded the lead alkyls.

Teflon columns had several advantages over pyrex. Teflon was stable to 260°C and was therefore suitable for the column material. Because teflon is not brittle, it was much easier to manipulate than glass columns. It also seemed to seal better against gas leaks than glass when teflon ferrules were used.

f. Second Set of Gasoline Samples

After the above modifications were made, a second set of gasoline samples were analyzed. These samples

were collected from various local gas stations. Premium, regular, and unleaded gasoline samples were analyzed for their lead content. Precision and resolution were increased (Figures 14a-18c).

The following experimental parameters were changed from the initial gasoline study.

1) The column length was increased from 30 inches stainless steel to 8 feet teflon.

2) The slit on the monochrometer was reduced from 150μ to 50μ.

3) The photomultiplier voltage was lowered from 620 V.D.C. to 400 V.D.C.

4) The sample volume was increased to 2 μL to improve precision.

With these modifications, the sensitivity of the instrument was improved 15 fold (ca. 10^{-10} g Pb per 1 μL sample volume). This was approximately 450 times greater than a similar A.A. flame detector for G.C.

5. Summary

A new atomic absorption detector for gas chromatography had been developed. The detector exhibited the excellent selectivity of atomic absorption while retaining the sensitivity of carbon atomizers. The sensitivity was approximately 10^{-10} g Pb per 1 μL sample volume or 450 times greater than a similar A.A. flame detector for G.C. Molecular background interference was negligible.

The G.C.-A.A. was able to separate the five lead alkyls in gasoline and relative retention times were established for them. Gasoline samples were characterized for lead

alkyl content. It was possible to recognize different brands of gasoline by the characteristic concentration patterns of the lead alkyl compounds.

C. GAS CHROMATOGRAPHY - ATOMIC ABSORPTION AS A NONSPECIFIC DETECTOR

1. Introduction

The unleaded gasolines showed significant absorption of the lead resonance lines but this proved to be organic in nature (Figures 19-23). These molecular signals can be distinguished from atomic signals with a continuum light source. When the temperature of the atomizer was increased, the absorption by the non-lead materials increased, indicating that the absorption was probably due to a combustion product rather than the incomplete combustion of the solvent molecules (Figure 24).

Absorption of the lead resonance line was detected from large concentrations of chlorine, nitrogen, and sulfur compounds in organic mixtures (Figures 25-28). This absorption was of interest because of the possibility of using the atomic absorption detector for a nonspecific detector. This phenomena had been demonstrated before in atomic absorption.[80]

Electron capture is a very sensitive detector system for gas chromatography. It is especially sensitive to functional groups with a high affinity for free electrons,[81] like the functional groups listed above. Unleaded gasoline samples were analyzed on G.C.-E.C.D. and compared to the

G.C.-A.A. analysis of the same (Figures 29-33).

2. Experimental Parameters

a. Gas Chromatography Parameters

1) Column - 1/8 inch diameter teflon, 8 feet long, packed with 20% tricresyl phosphate on Chromosorb W (Teklab, Inc.)

2) Carrier gas - Argon (35 cc/min)

3) Column temperature - 100°C

4) Injection port temperature - 100°C

5) Transfer line temperature - 110°C

b. Atomic Absorption parameters

1) Lamp current - 8 mA

2) High voltage - 500 V.D.C.

3) Slit width - 50 microns

4) Analytical wavelength - 283.3 nm

5) Atomizer Temperature - 1800°C

6) System was modulated

c. Equipment

1) G.C.-A.A. described earlier

2) G.C.-E.C.D. - Perkin-Elmer Model 3920 Gas chromatograph with Ni^{63} E.C.D. source

d. Chemicals

1) Unleaded gasoline samples - donated by area gas stations

2) Hexane

3) 1-Chloro-2-methyl propane

4) Chlorobenzene

5) n-Butanethiol

6) Tripropylamine

7) Phenyl isothiocyanate

8) Tri-n-butyl phosphate

3. Procedure

Unleaded gasoline samples were collected at area gas stations. Samples of the different gasolines were injected into the G.C.-A.A. and analyzed for alkyl lead content. Retention times were noted for various molecular species in the unleaded gasoline. These same samples were then analyzed on G.C.-E.C.D. and compared to the G.C.-A.A. analysis.

One unleaded gasoline sample was then chosen and was run at different atomization temperatures and the absorption compared.

Dilutions of 1-chloro-2-methyl propane, chlorobenzene, n-butanethiol, tripropylamine, phenyl isothiocyanate, and tri-n-butyl phosphate in hexane were made. These samples were also run with the lead hollow-cathode lamp.

After analysis on the G.C.-A.A., the lead hollow-cathode was replaced by a deuterium lamp, and the entire group of samples was re-run to determine the molecular background absorption.

4. Results and Discussion

When low-lead and unleaded gasolines were first introduced, traces of lead compounds were found in them.

The source of these lead compounds was probably lead alkyls from the leaded gasolines that previously occupied the storage tanks at the gas stations. It was noted that the lead concentrations were within the government's allowable levels.

After several months, lead compounds were no longer detected in unleaded gasolines. It was presumed that the traces of lead originally observed had been effectively scavanged from the storage tanks by some of the components of the unleaded gasoline.

Several nonlead compounds gave molecular absorption of the lead resonance lines (Figures 19-23). During an atomizer temperature versus atomization efficiency study (Figure 24), it was noted that above 2000°C, molecular absorption increased with increasing temperature. The increased molecular absorption was obviously due to combustion of solvent molecules.

The unleaded gasoline samples were then run on a G.C. with an electron capture detector to determine if the absorbing compounds might contain electronegative functional groups. The G.C.-E.C.D. chromatograms for unleaded gasolines were very similar to the molecular absorption of unleaded gasolines at high atomizer temperatures (Figures 29-33).

Compounds with various functional groups were chosen to determine if the G.C.-A.A. system could be used as a nonspecific detector. The compounds chosen for analysis

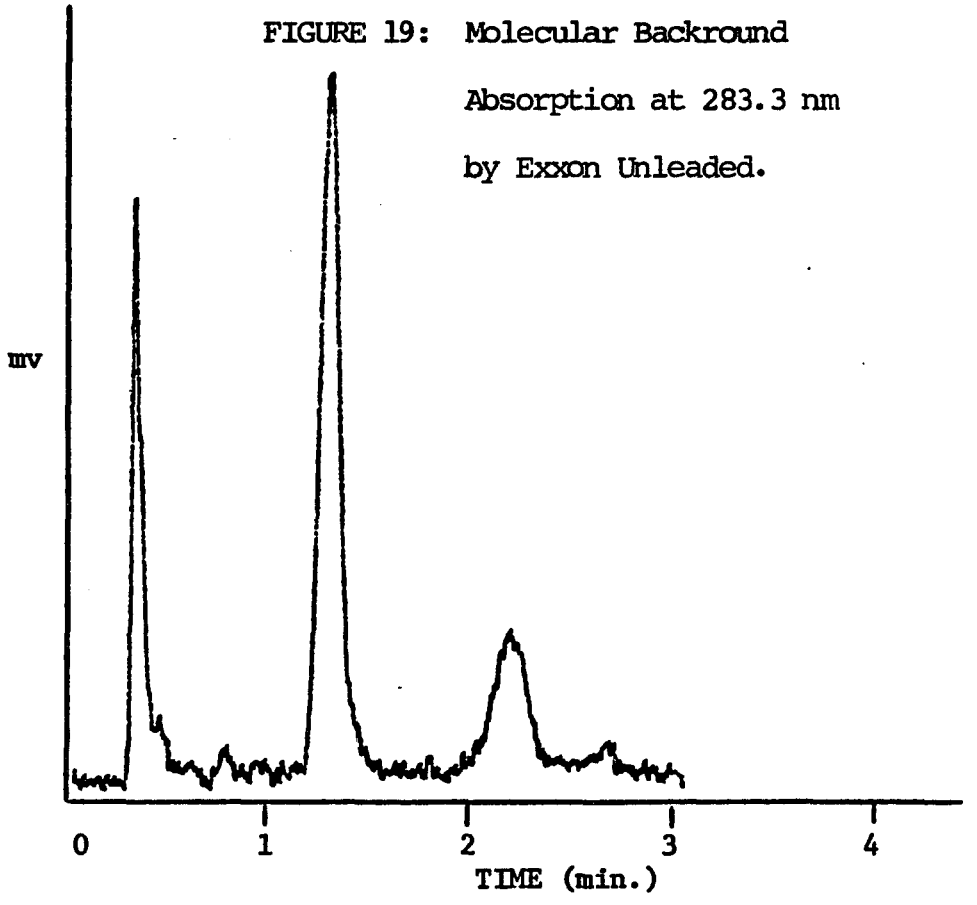


FIGURE 19: Molecular Backround Absorption at 283.3 nm by Exxon Unleaded.

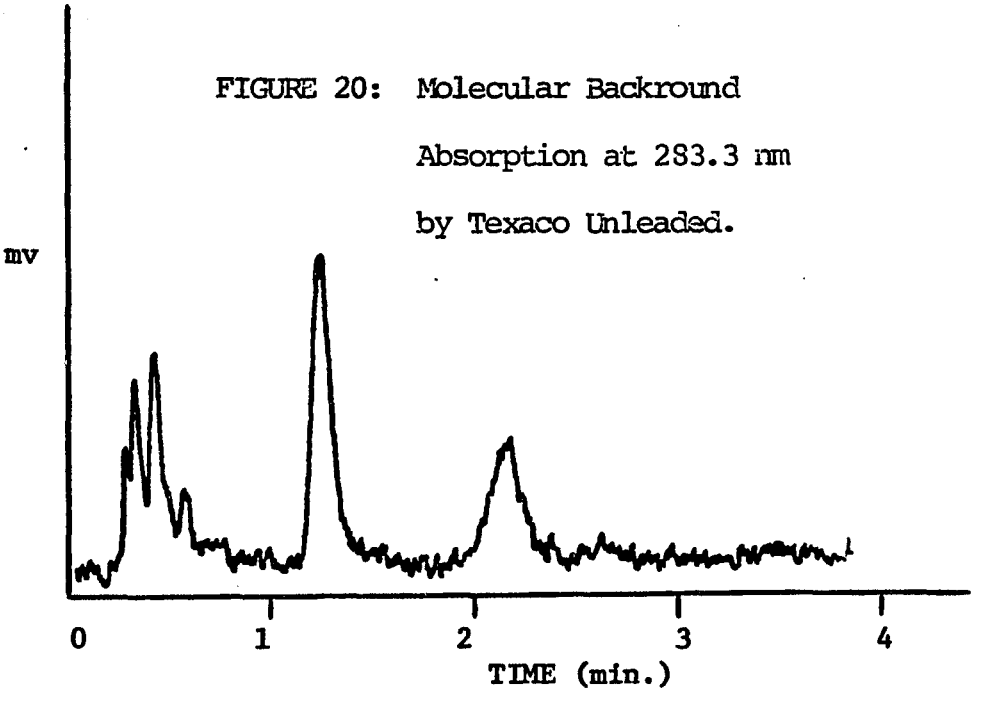


FIGURE 20: Molecular Backround Absorption at 283.3 nm by Texaco Unleaded.

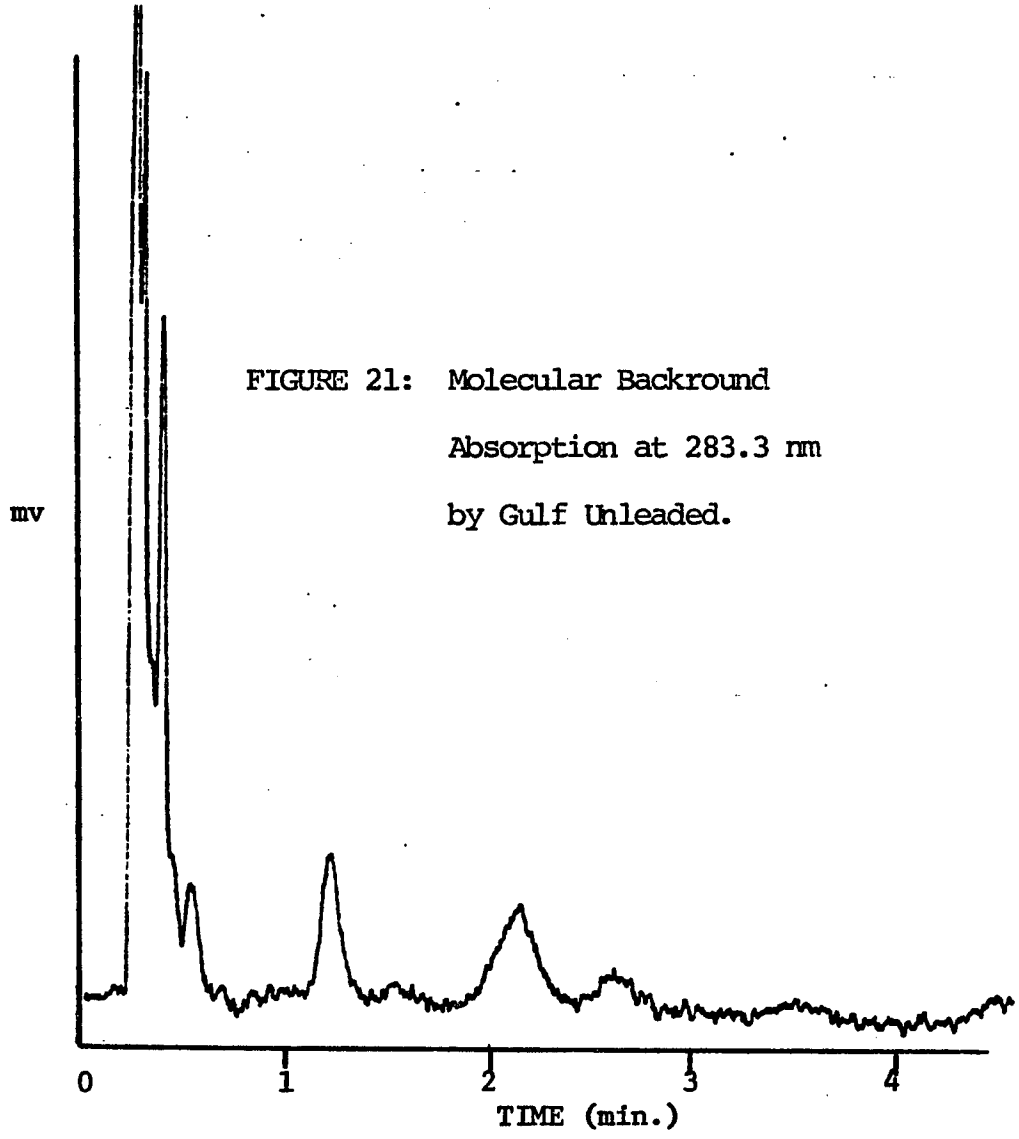


FIGURE 21: Molecular Backround Absorption at 283.3 nm by Gulf Unleaded.

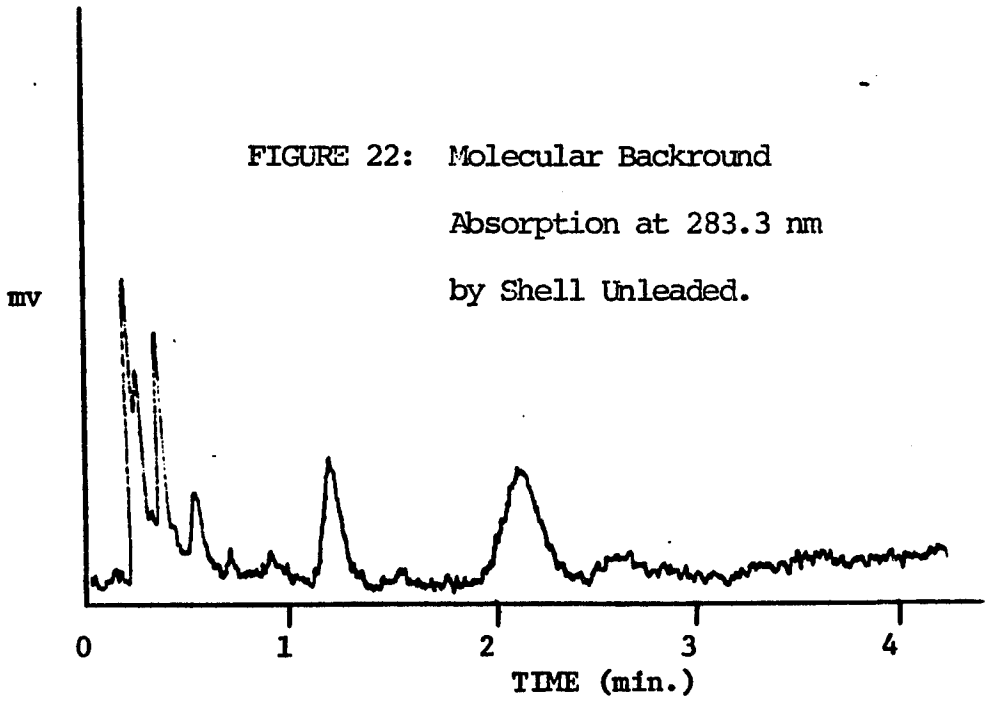


FIGURE 22: Molecular Backround Absorption at 283.3 nm by Shell Unleaded.

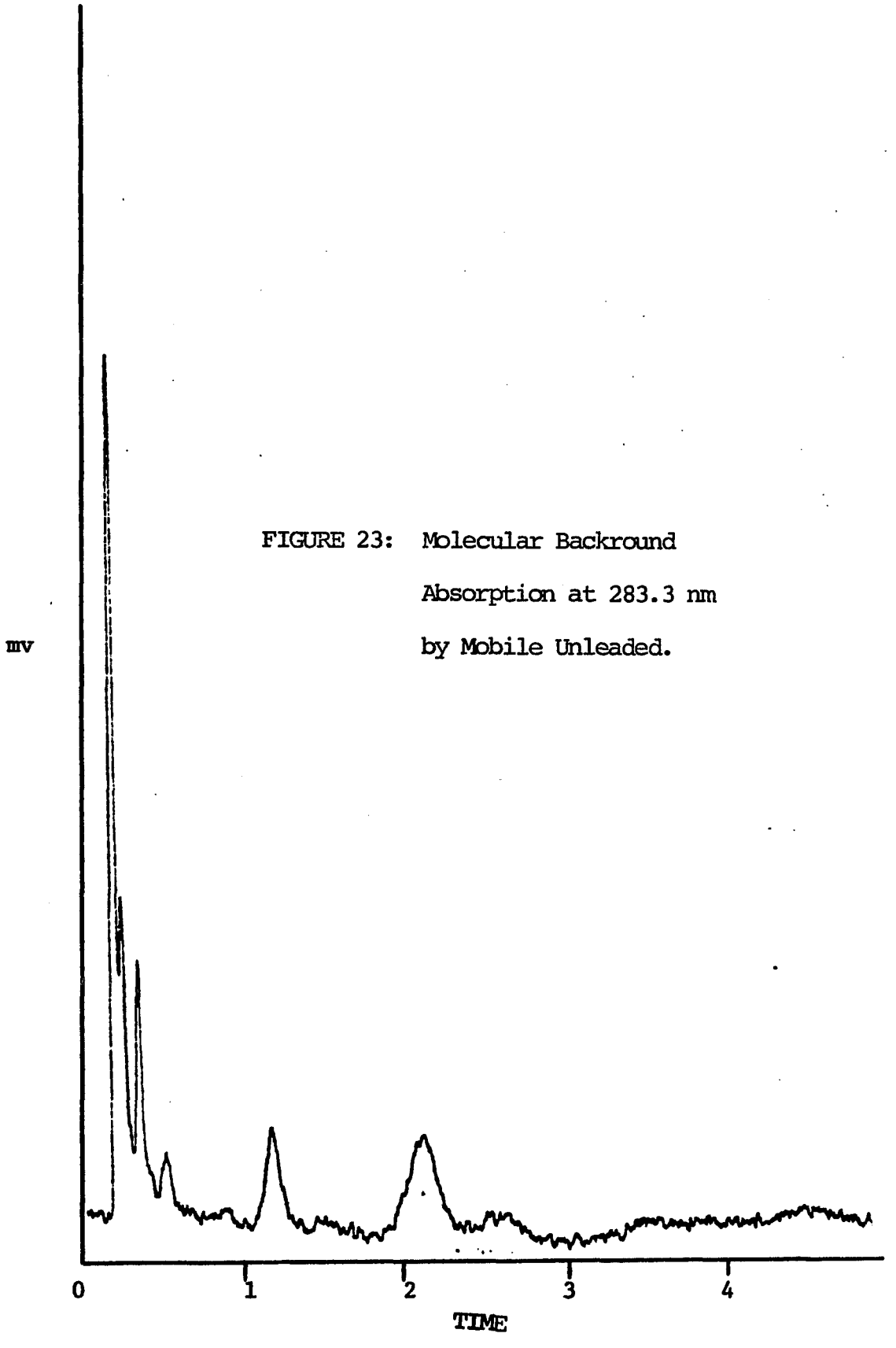


FIGURE 23: Molecular Backround Absorption at 283.3 nm by Mobile Unleaded.

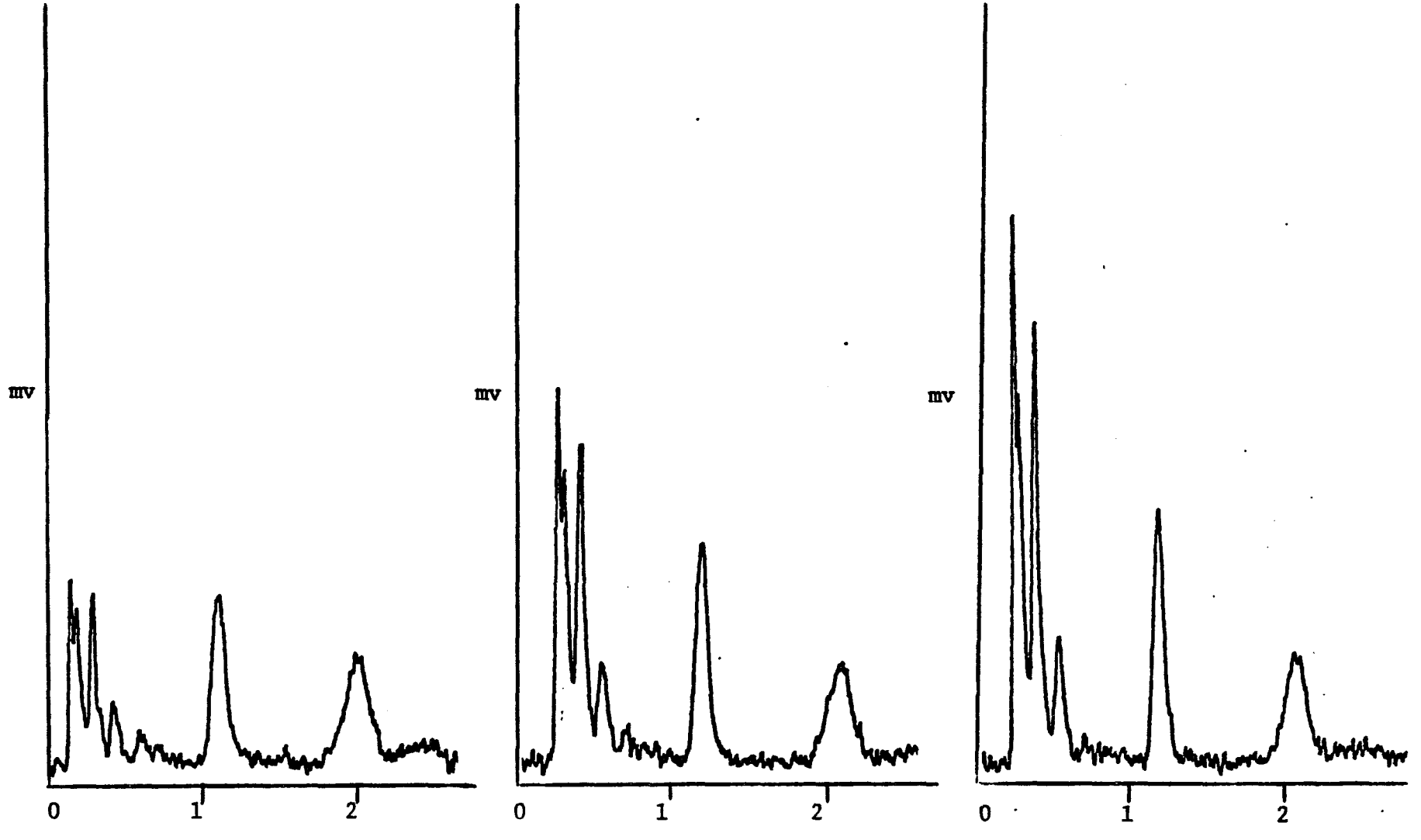


FIGURE 24: Increased Molecular Absorption with Increasing Atomizer Temperature

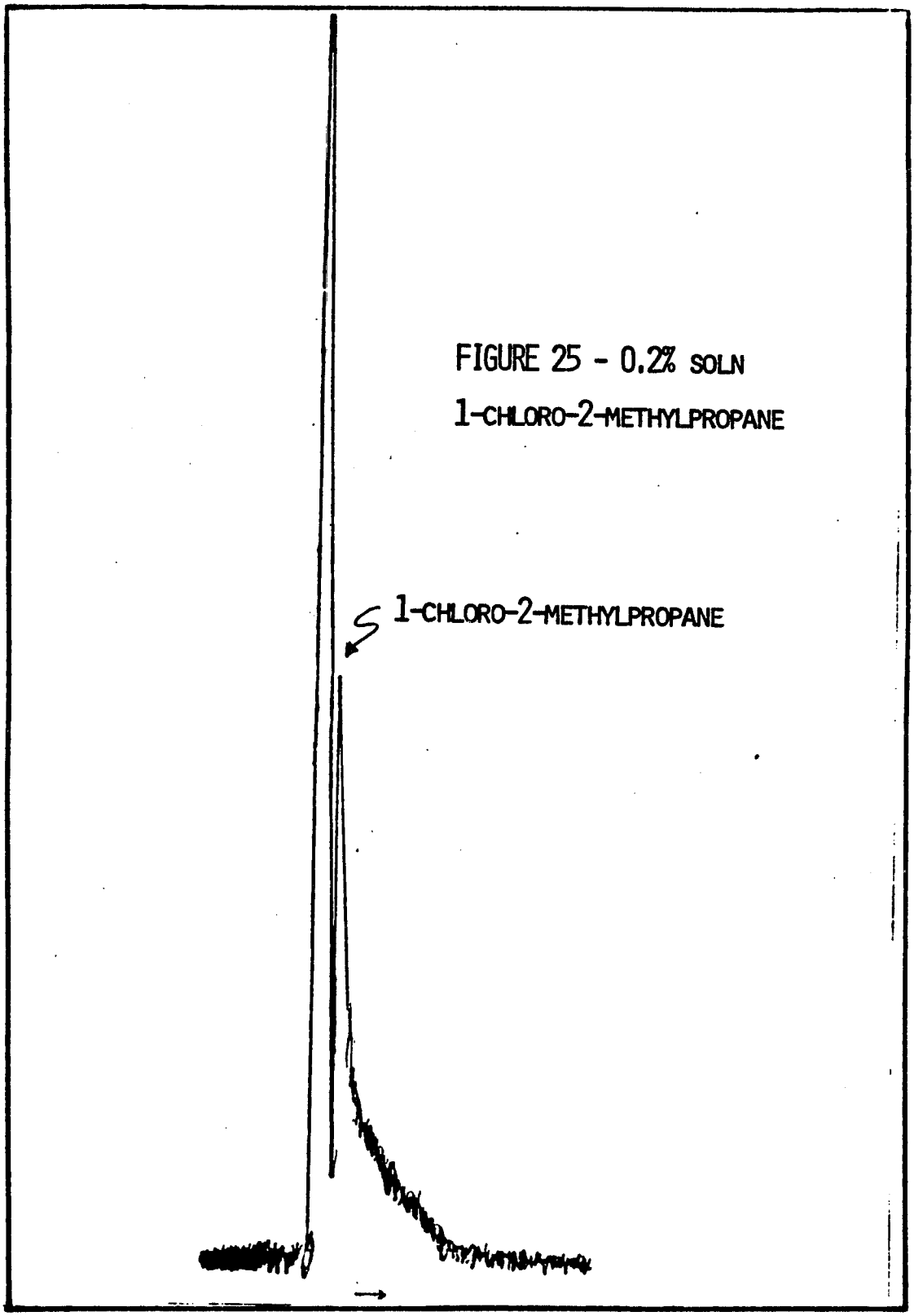


FIGURE 25 - 0.2% SOLN
1-CHLORO-2-METHYLPROPANE

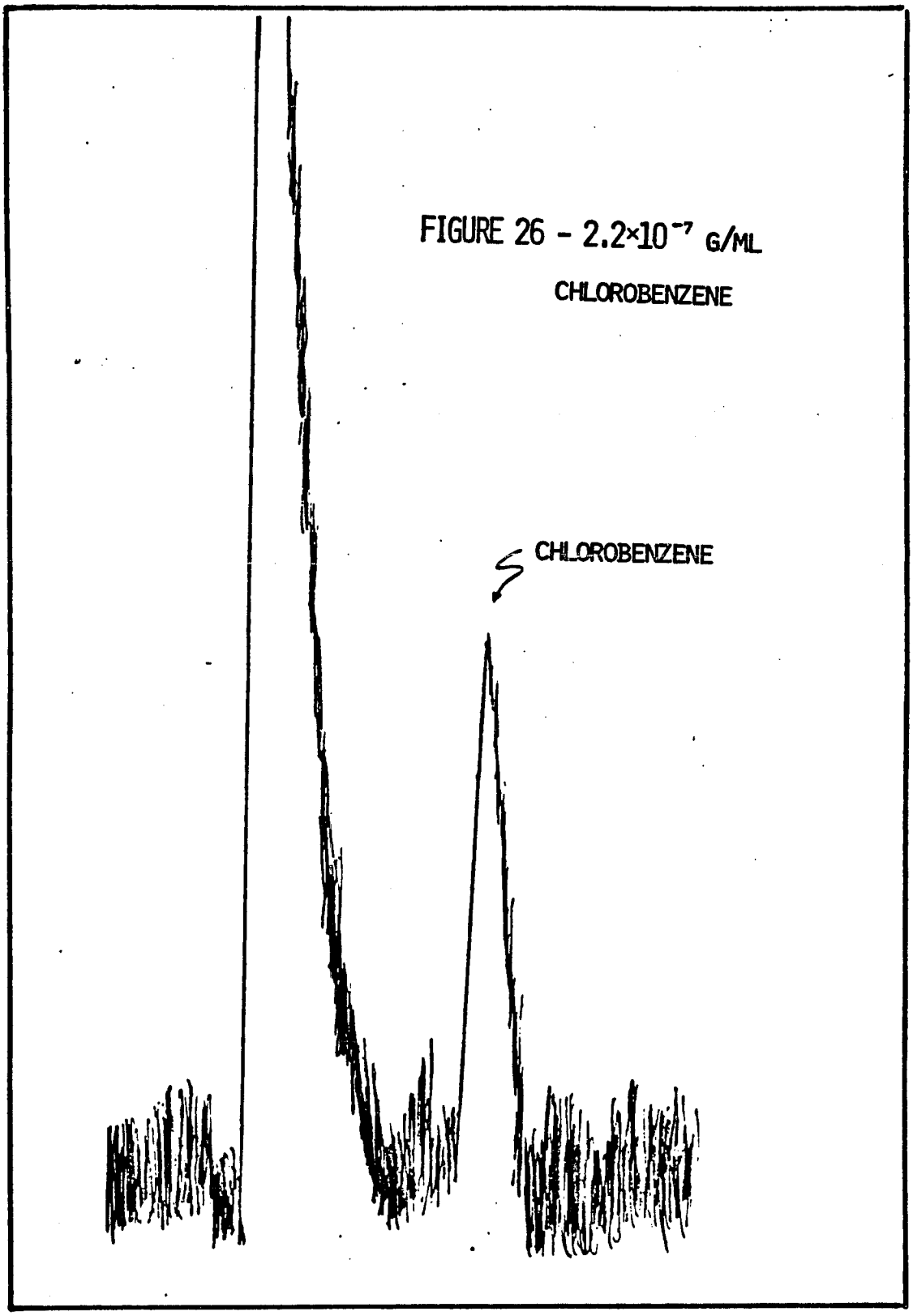


FIGURE 26 - 2.2×10^{-7} G/ML CHLOROBENZENE

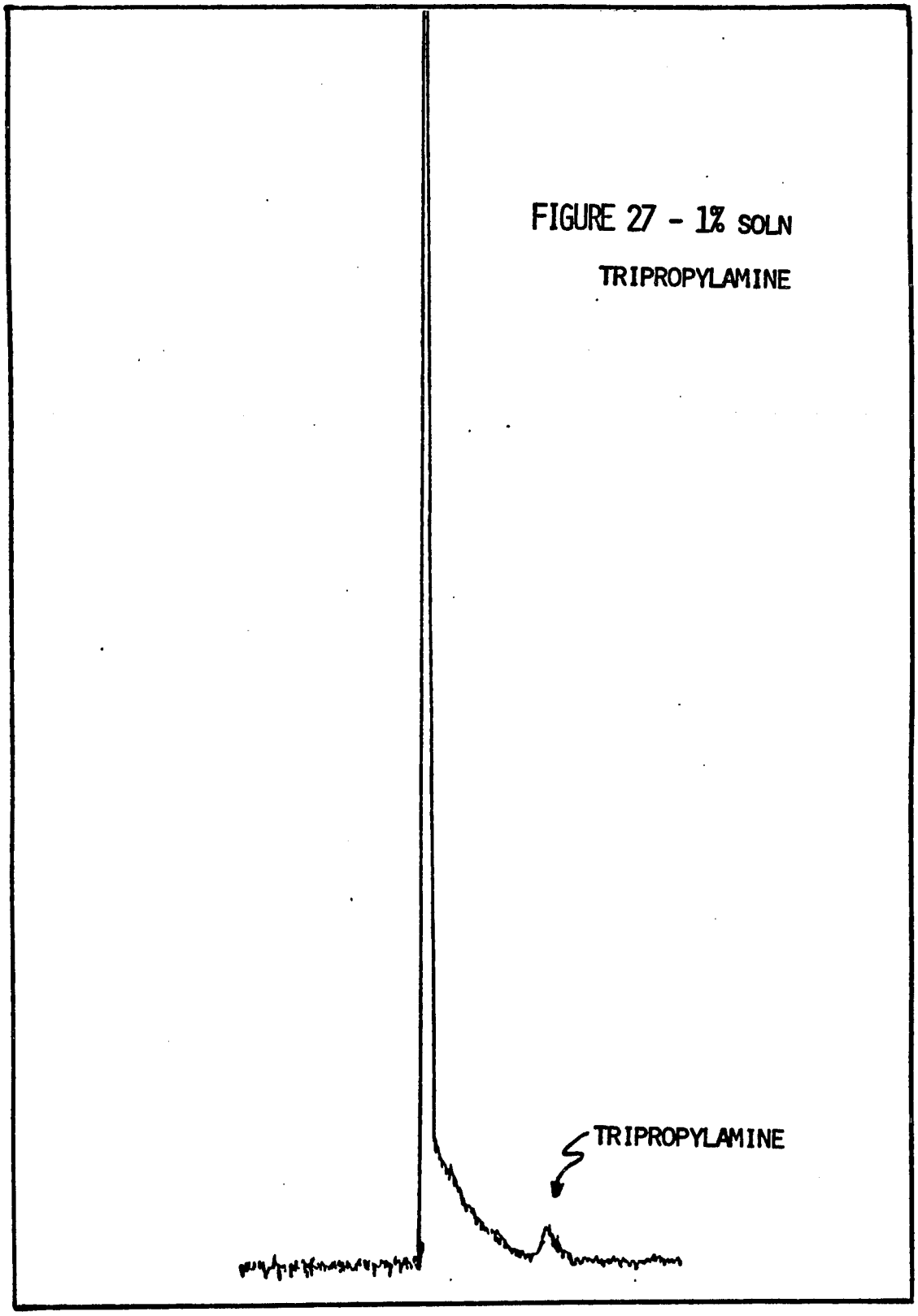


FIGURE 27 - 1% SOLN

TRIPROPYLAMINE

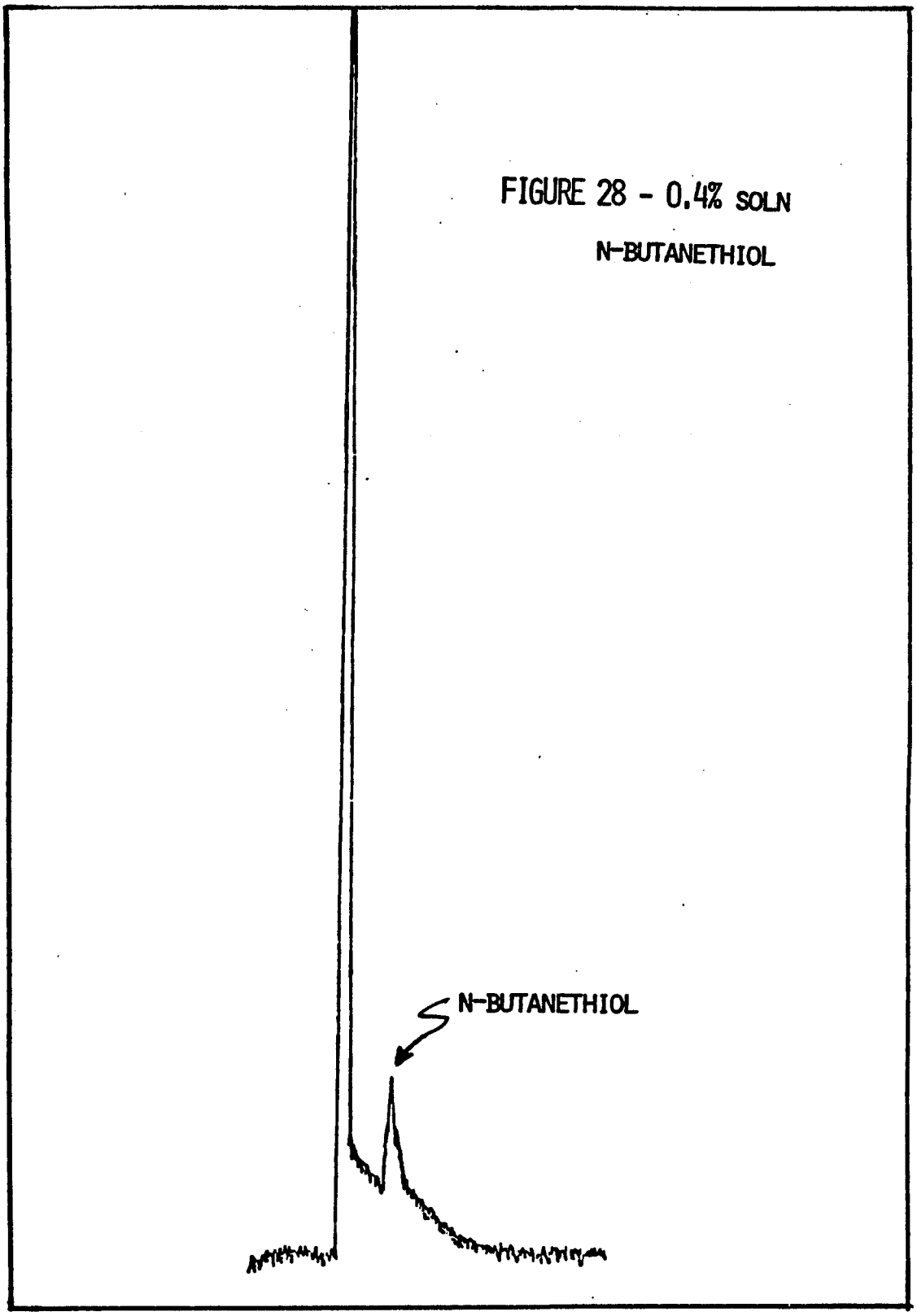


FIGURE 28 - 0.4% SOLN
N-BUTANETHIOL
N-BUTANETHIOL

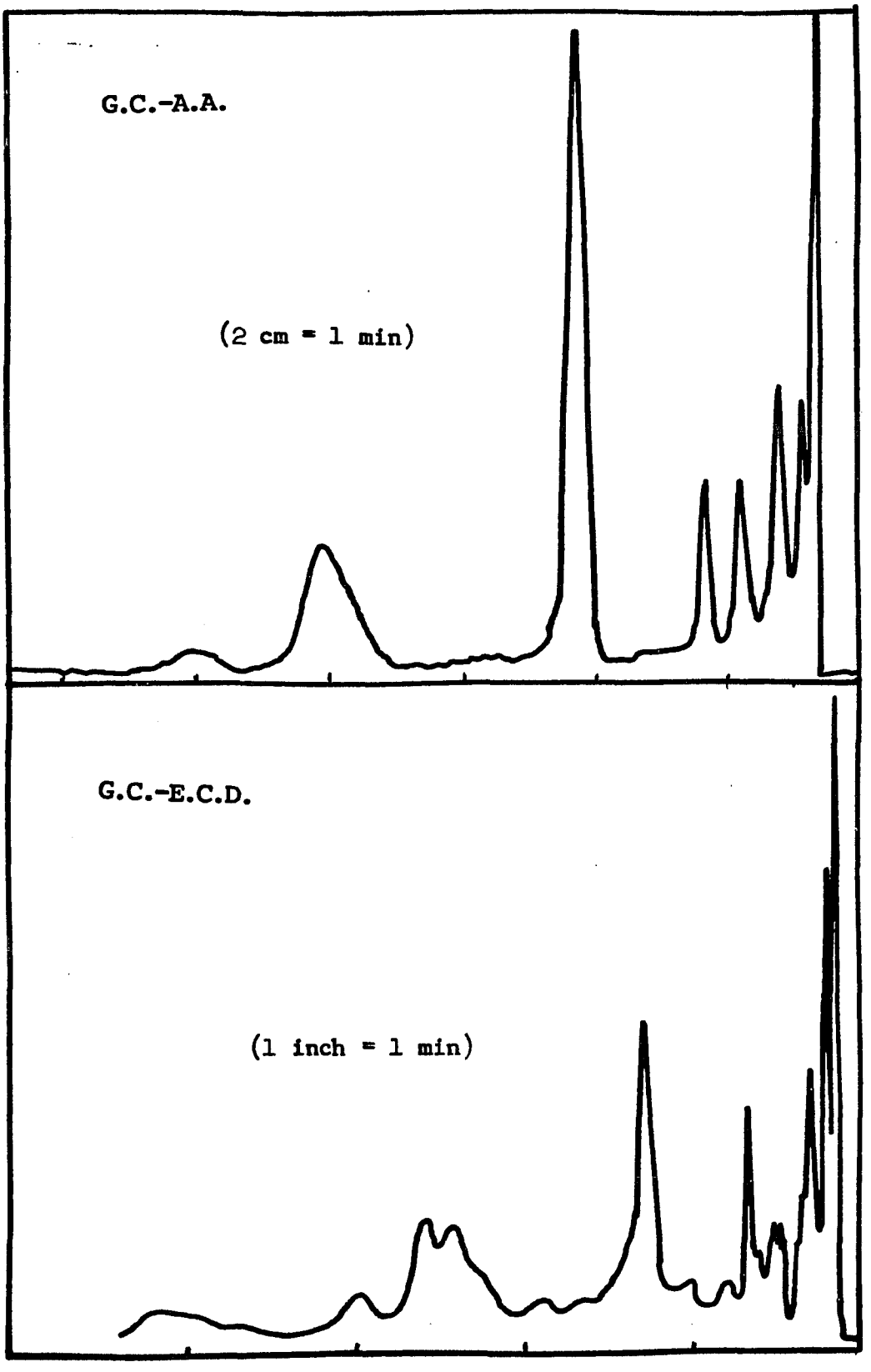


FIGURE 29: G.C.-A.A. vs. G.C.-E.C.D., Exxon Unleaded.

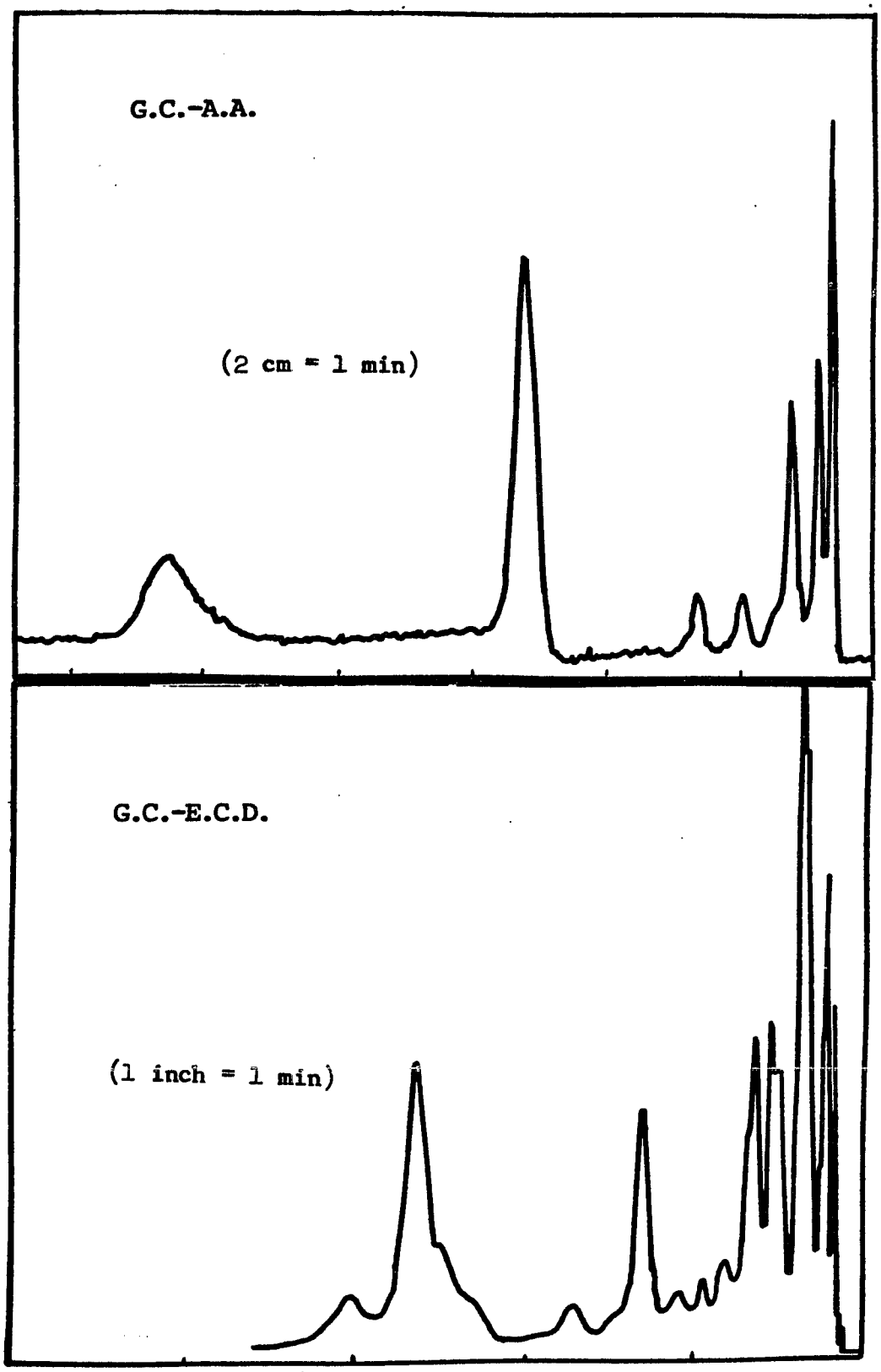


FIGURE 30: G.C.-A.A. vs. G.C.-E.C.D., Texaco Unleaded.

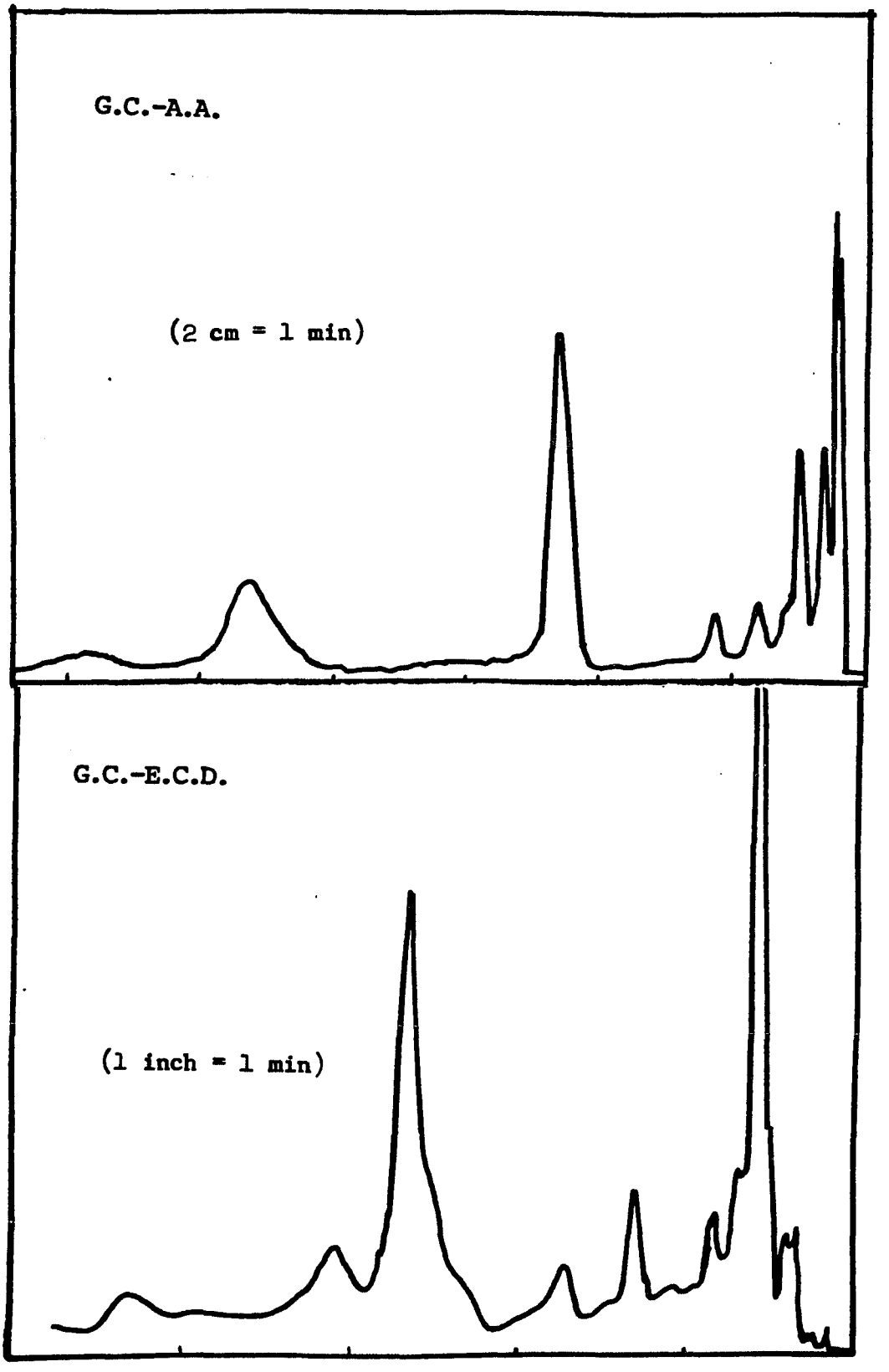


FIGURE 31: G.C.-A.A. vs. G.C.-E.C.D., Gulf Unleaded.

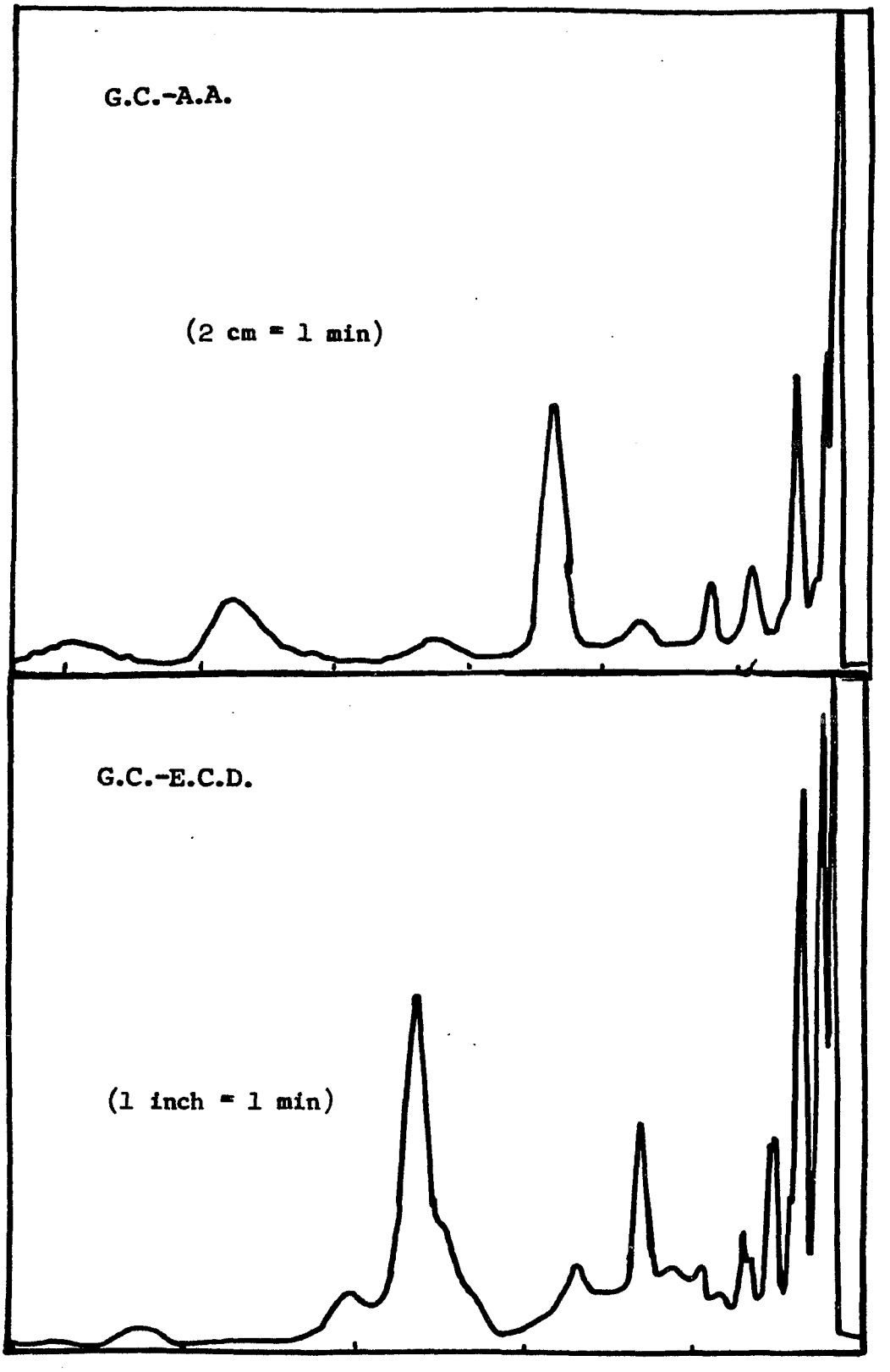


FIGURE 32: G.C.-A.A. vs. G.C.-E.C.D., Shell Unleaded.

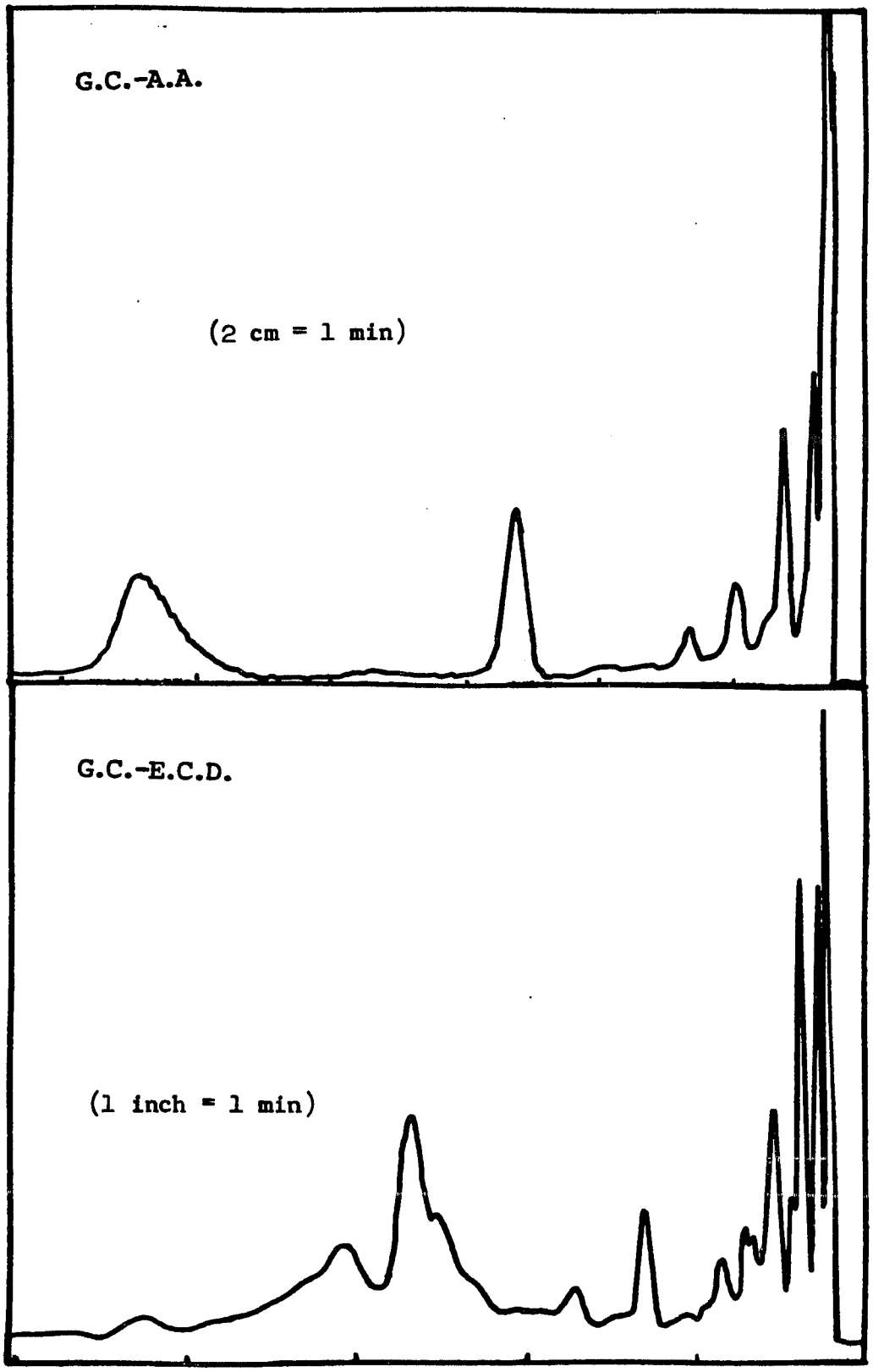


FIGURE 33: G.C.-A.A. vs. G.C.-E.C.D., Mobile Unleaded.

had functional groups that represented an alkyl halogen, an aromatic halogen, an amine, and an alkyl thiol. No absorption was noted for phosphate or thiocyanate compounds. Absorption of the lead 283.3 nm line was noted for the following organic compounds (a) 1-chloro-2-methyl propane as a 0.2% solution, (b) chlorobenzene as a 2.2×10^{-7} g/mL solution, (c) tripropylamine as a 1% solution (d) n-Butanethiol as a 0.4% solution.

5. Summary

The gas chromatography-atomic absorption system has been utilized as a nonspecific detector. The G.C.-A.A. analysis of unleaded gasolines compares favorably to G.C.-E.C.D.

Organic compounds with various functional groups were analyzed and it was found that alkyl and aromatic halogens, amines, and thiols absorb the lead 283.3 nm line. Except for the aromatic halogen compound, the G.C.-A.A. lacks the sensitivity to be routinely used as a nonspecific detector.

The molecular absorption of these compounds was very dependent upon the atomization temperature. As the atomization temperature increased, the molecular absorption increased correspondingly, indicating that the actual absorbing species was a combustion product and not the undecomposed compound.

D. A NEW MODIFIED ATOMIC ABSORPTION DETECTOR

1. Introduction

A new atomic absorption detector was designed and built. The new detector is a modified version of the original atomic absorption detector. Modifications were designed to improve the stability and usefulness of the detector.

The usefulness of the A.A. detector is mainly a function of the lifetime of the resistance heated carbon element. In the original detector the carbon element lasted approximately 24 hours of continuous use. Deterioration occurred from the outside. The G.C. column carrier gas also served as the detector purge gas. The detector was not sealed in order that the purge gas could escape. This, however, allowed air to leak back into the detector. Air coming into contact with the hot carbon element was believed to cause the rapid deterioration of the carbon piece.

The following modifications were proposed to prolong the lifetime of the resistance heated carbon element:

1) The use of O-rings to seal surfaces to stop air leaks

2) An auxillary argon purge to force an increased argon flow around the outside of the carbon element.

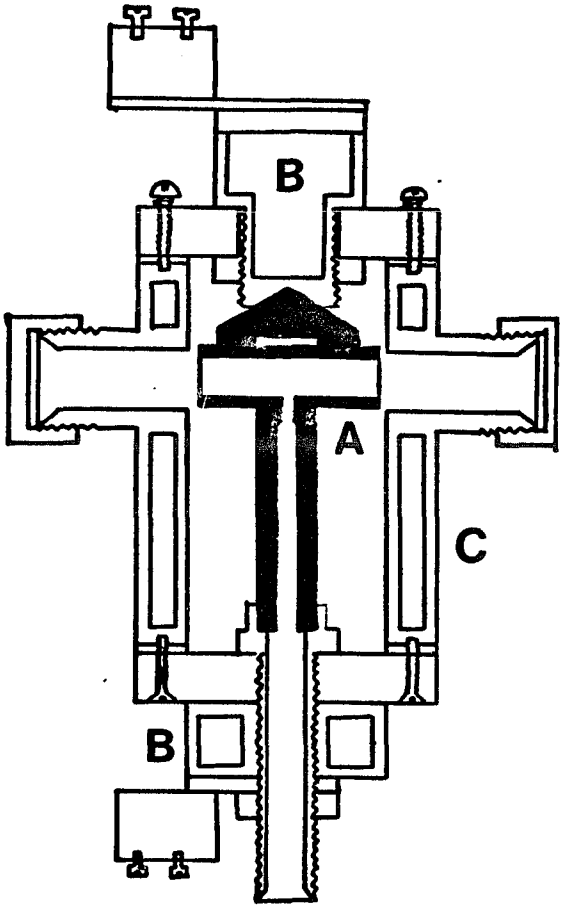
3) Addition of 5.0%-10.0% methane to the argon carrier gas and to the auxillary argon purge gas for methane pyrolysis to make a more resistant surface on the carbon element.

2. The New Design

The new detector has design features to improve the lifetime of the carbon element. In addition, the detector was designed to allow for a longer atomization path and less carbon waste at the top electrode.

The new detector (Figure 34) was constructed from stainless steel. It consisted of a water cooled stainless steel jacket. Two water cooled electrodes supported the carbon resistance element. The lower electrode was hollow to allow connection of a heated transfer line from the gas chromatograph to the atomizer. The transfer line was sealed to the atomizer by means of a special teflon ferrule. The water cooled electrodes were connected to the low voltage side of the stepdown transformer by means of 2 No. 0 welding cables.

Problems were almost immediately noted at the carbon element-electrode junction. The expansion properties of the carbon and the stainless steel were sufficiently different to cause problems with arcing inside the atomizer. As the carbon element heated, the carbon-stainless steel connection weakened and arcing began. Stainless steel was actually sputtered off of the electrodes. In the areas where arcing occurred, cracks in the stainless steel were noted. This is probably due to the fact that stainless steel becomes work hardened and brittle when heated and cooled as in the temperature cycle of the atomizer when it is turned on and off in the course of normal operation.



A. Carbon Resistance Element

B. Water-cooled Electrodes Supporting Resistance Element

C. Water-cooled Atomizer Housing

FIGURE 34: Schematic Diagram of Modified G.C.-A.A. Detector

The top and bottom electrodes were replaced by brass electrodes. This resolved the arcing problem. It was also noted that less power was required to heat the carbon element (∿1500 watts).

The top and bottom electrodes were separated from the body of the atomizer by 2 teflon washers. These washers helped to seal the atomizer against air leaks. The top electrode was mounted in the top plate which was made of transite. An O-ring sealed the electrode in place. The top electrode was spring loaded so that it would make good contact with the carbon element.

An opening through the wall of the atomizer body was designed to allow an auxiliary argon purge. The auxiliary argon purge around the carbon element was needed to remove air that leaked into the atomizer and was trapped in the dead spaces of the atomizer. By adding methane to the auxiliary purge, a pyrolytic surface could be coated on the carbon element and make it more resistant against deterioration from air.

Initially it was noted that the sensitivity of the new atomizer was not as low as the old atomizer. It was then discovered that the atomizer was sealed too well causing a build-up of pressure inside the atomizer and a decrease of sample flow through the atomizer. By slightly loosening the top plate of the atomizer to allow argon to escape, sensitivity was restored.

Without the aid of an auxiliary purge or a pyrolytic

graphite coat, the lifetime of the resistance heated carbon element was doubled to approximately 50 continuous hours of operation.

3. A Comparison of Carbon Element Designs

Two basic carbon designs have been used for the carbon elements, a modified "hollow T" and a "hollow I". The "hollow T" had an extended heated light path that the "hollow I" did not have. The extended heated light path seemed to lower the sensitivity limit by a factor of 2.0. The difference in sensitivity was made up in the construction time required to make the graphite elements. The original "T" required approximately 20 minutes per element whereas the "I" required less than 10 minutes for construction. The final "T" that was being used required approximately 15 minutes for construction. If the crosspieces were recycled so that only a new atomization chamber was needed, a new carbon element could be made in 5 minutes.

All "T" pieces required the crosspiece to be glued to the atomization chamber. This was accomplished by adding one drop of furfuryl alcohol to the carbon-carbon junction and then adding one drop of concentrated hydrochloric acid or concentrated sulfuric acid to the junction. The concentrated acid polymerized the alcohol which made a very good seal.

The following key features of the carbon element were required for efficient atomization and sufficient

sensitivity:

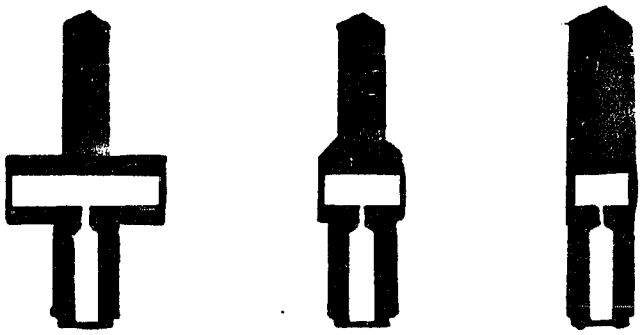
1) An extended light path can improve the efficiency of atomization and thereby improve sensitivity.

2) The volume of the atomization chamber is not critical as long as it tapers before entering the light path.

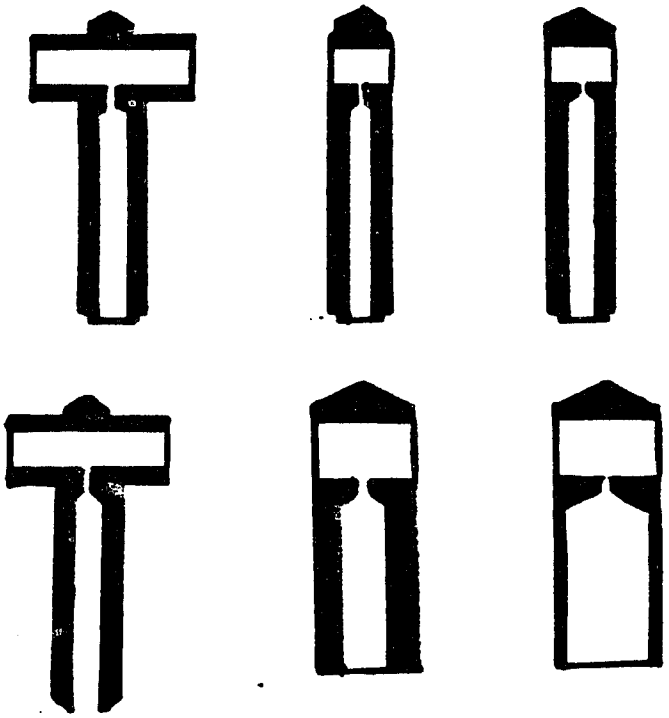
It was presumed that the tapering increased sample contact with the graphite before the sample entered the light path. The hot graphite catalyzed the formation of the free atomic species.[77] Very large volumes of the atomization chamber lowered sensitivity due to a decrease in graphite surface area per unit quantity of sample. The various carbon element designs are shown in Figure 35.

After 24 hours of continuous use, a "hollow T" was broken apart and examined. The botton 1/3 of the inside surface was shiny gray in color indicating that a pyrolytic coat had formed. This pyrolytic coat could only form from the decomposition of organic samples. The upper 2/3 of the atomization chamber showed only minor deterioration that was expected from normal use. This observation indicated that complete sample decomposition occurred in the lower portion of the atomization chamber.

As the "hollow T" aged, the junction between the atomization chamber and the cross piece loosened and heating of the cross piece was irregular. It was not uncommon for the center of the crosspiece to be hot and the ends to be several hundred degrees cooler. A new "hollow T" was designed (Figure 36). To insure even heating of the cross-



Carbon Elements for Original G.C.-A.A.



Carbon Elements for Modified G.C.-A.A.

FIGURE 35: A Comparison of Carbon Element Designs

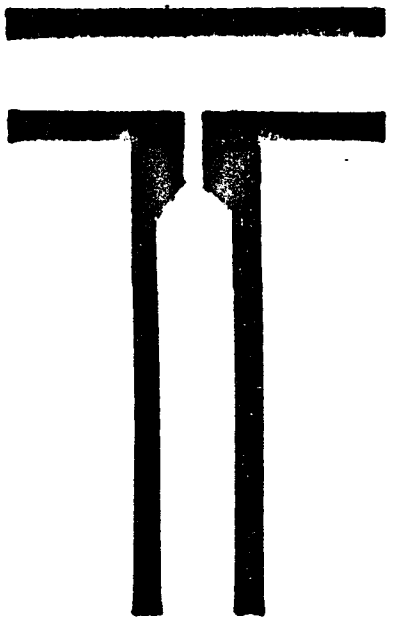


FIGURE 36: New "Hollow T" Carbon Element

piece a graphite cap was designed that made electrical contact between the ends of the crosspiece and the top electrode (Figure 37). The graphite cap served 2 purposes. (a) It insured that the ends of the crosspiece were heated, in that the new "T" made a 3 point electrical attachment to the top and bottom electrode. (b) Because of the thickness of the graphite cap, the brass electrode-graphite junction was maintained at a much lower temperature.

4. Column Efficiency vs. Atomization Efficiency as a Function of Flow Rate

The number of theoretical plates (N) or more accurately the theoretical plate height (H) is often used as a measure of column efficiency (Equation 2). The optimum flow rate ($\bar{u}$) to produce a Gaussian distribution is determined by a van Deemter plot (i.e., H vs. $\bar{u}$). Peak area can be taken as a measure of the atomization efficiency (i.e., the number of free atoms capable of absorbing radiation in the light path is proportional to the peak area of the chromatogram).

A 100 ppm Pb solution as TEL (1 µL sample volume) was repeatedly injected into the G.C.-A.A. An 8 foot long tricresyl phosphate column was used. All variables were held constant except the flow rate ($\bar{u}$), which was changed before each run. Flow rates from 30 to 140 mL/min were used. Two plots were made, H vs. $\bar{u}$ and Peak area vs. $\bar{u}$ (Figure 38).

The van Deemter plot indicated an optimum flow rate of 80 mL/min. Atomization efficiency was maximum at 30 mL/min.

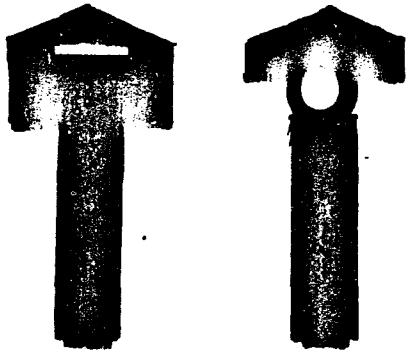
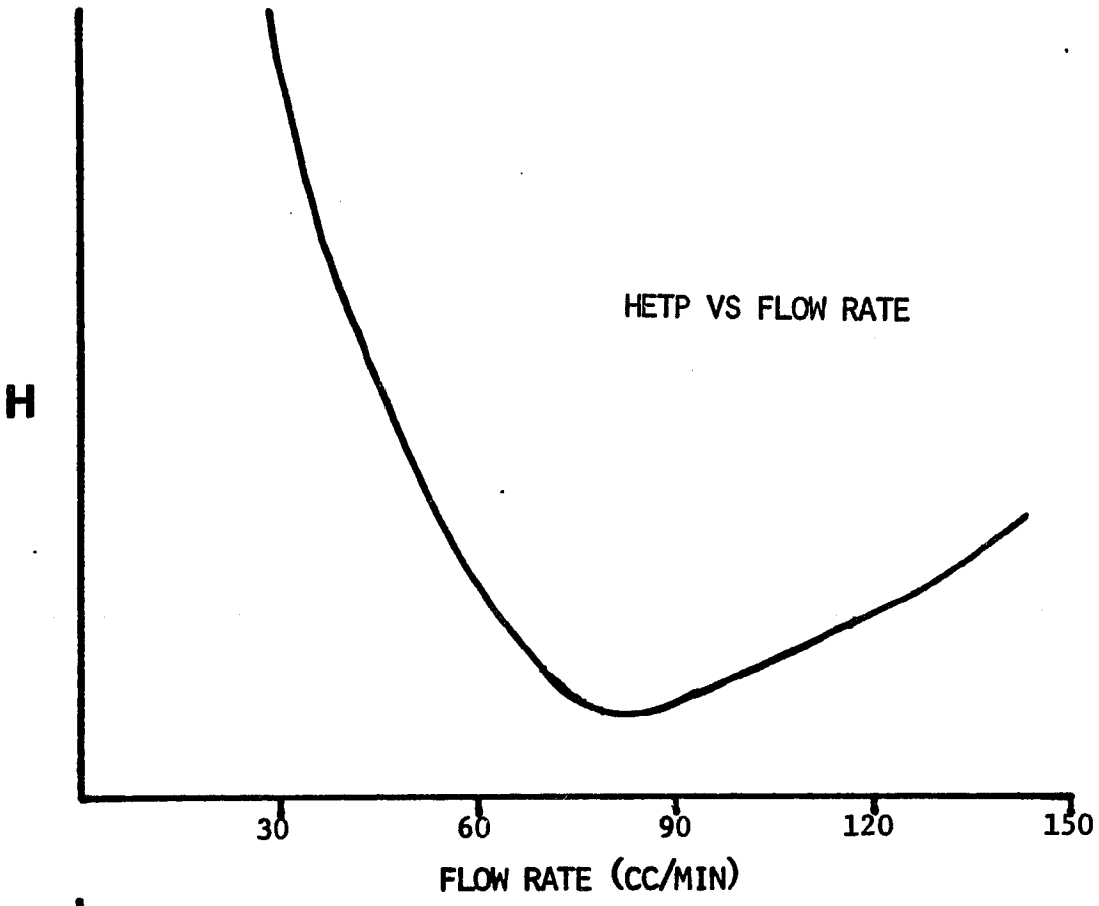


FIGURE 37: Graphite Cap for New "Hollow T" Carbon Element



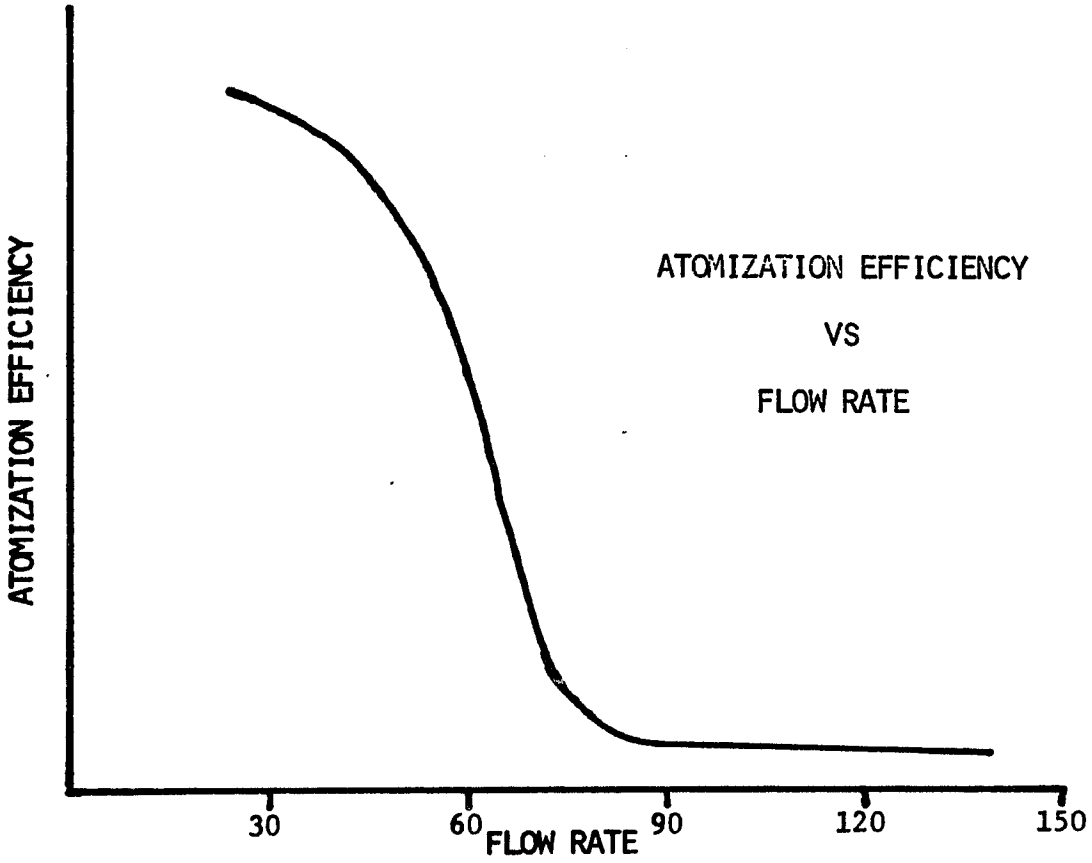


FIGURE 38: G.C. Flow Rate vs. HETP and Atomization Efficiency

This was an interesting observation.

For each compound and different column that is used, a van Deemter plot and atomization efficiency versus flow rate plot should be made to determine the optimum operating conditions for an analysis. These 2 variables should be optimized though they might be different.

5. Summary

A new modified atomic absorption detector was designed and built for the G.C.-A.A. The new design incorporated mechanisms of improving the stability and prolonging the usefulness of the resistance heated carbon element.

The design of the carbon element was studied. Criteria were determined for maximum atomization efficiency.

The optimum flow rate for the new G.C.-A.A. detector should be determined from both a van Deemter plot and an atomization efficiency versus flow rate plot.

E. EVAPORATION OF GASOLINE

1. Introduction

Previous studies have shown that relatively high concentrations of molecular lead are present in the atmosphere.[82] The EPA definition of molecular lead is that material which will pass through a 0.45 micron filter. The data referred to above were achieved using a 0.01 micron filter which would eliminate a great majority of small sized particulate material. The equipment used was

capable of very rapid determination on small quantities of air. Samples could be analyzed every five minutes.

Other workers used scrubbing agents followed by methods of concentration of the scrubbing solution. This involved long scrubbing times that lasted several hours.[83] The concentrations of lead detected were the averages of those experienced for the total time of scrubbing. Peak concentrations could be easily obscured by averaging out with concentrations at non-peak times. In general these results have not been as high as those detected in the former studies.

A major source of error in a majority of molecular lead determinations was a preconceived notion that molecular lead must be organic in nature.[84] It has been assumed that since the vapor pressure of inorganic lead compounds is very low that molecular lead cannot be inorganic in nature. Scrubbing agents that will remove organic lead were therefore sufficient for the determination of molecular lead in the atmosphere. A scrubbing agent efficient for organic compounds may indeed be very inefficient for inorganic lead. This was a self-sustaining and self-deceiving argument.

It has been assumed that the majority of molecular lead is evolved from evaporating gasoline.[2] The lead alkyls of gasoline have a sufficient vapor pressure to volatilize into the atmosphere. It is known that gasoline evaporates from automobile gas tanks and carburetors,

particularly during start-up. The rate of evaporation of lead alkyls from gasoline depends on the partial pressure of the lead alkyl components under the condition of evaporation. Vapor pressures of these compounds suggest that they may not be amongst the first components to evaporate from gasoline.

If total evaporation of gasoline occurs then obviously TEL will find its way into the atmosphere and become a pollutant. However if a tank of gasoline is allowed to evaporate and a cup full of gasoline evaporates off, then the amount of tetraalkyl leads finding their way into the atmosphere will depend upon their partial pressures.

The evaporation process of tetraalkyl leads from gasoline was studied. The study is described below.

2. Experimental Parameters

a. Equipment

1) G.C.-A.A. as previously described

2) Gasoline distillation system (Figure 39)

b. Gas Chromatography Parameters

1) Column - 1/8 inch diameter teflon, 8 feet long, packed with 20% tricresyl phosphate on Chromosorb W (Teklab, Inc.)

2) Carrier Gas - Argon (35 cc/min)

3) Column temperature - 100°C

4) Injection port temperature - 100°C

5) Transfer line temperature - 110°C

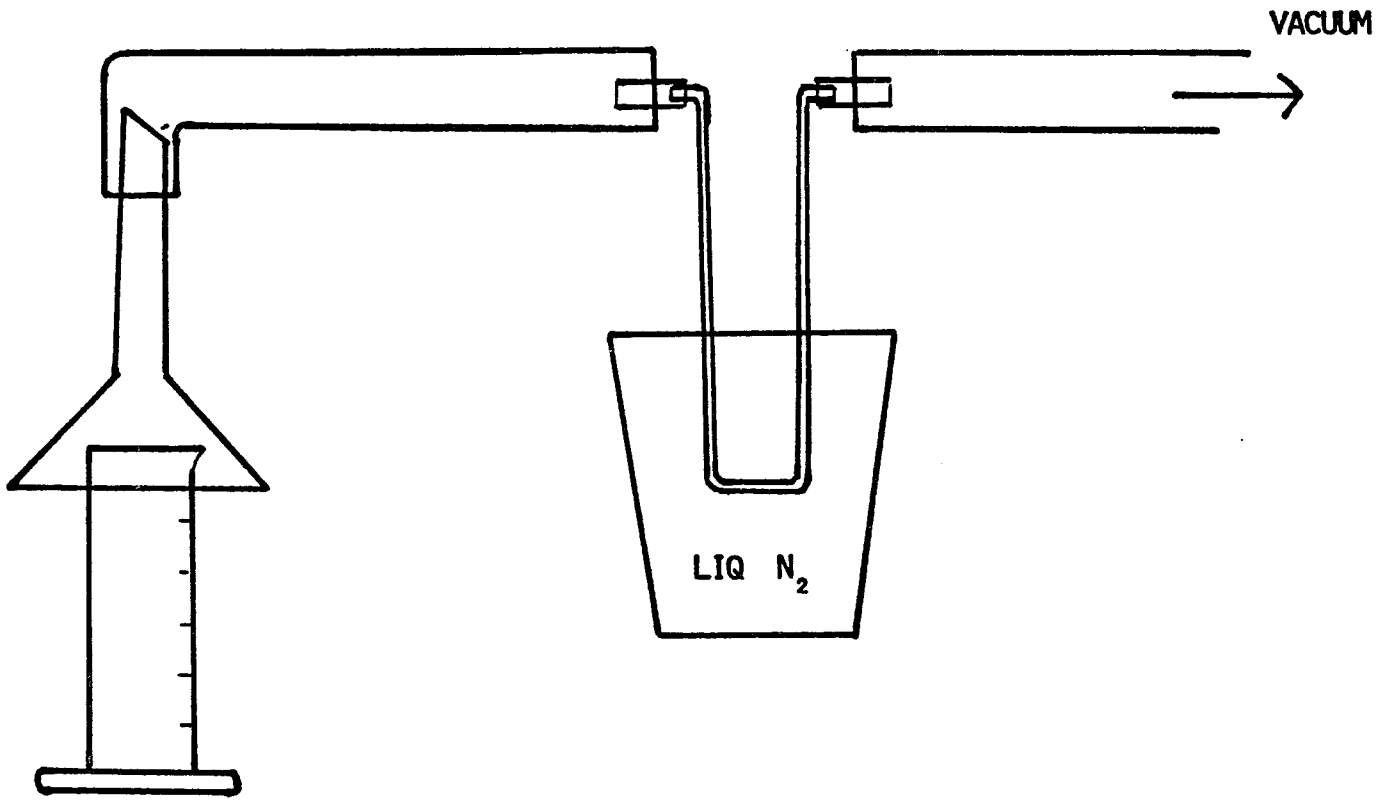


FIGURE 39: Schematic Diagram of Gasoline Distillation System

c. Atomic Absorption Parameters

1) Lamp current - 8mA

2) High voltage - 500 V.D.C.

3) Slit width - 50 microns

4) Analytical wavelength - 283.3 nm

5) Atomizer temperature - 1800°C

6) System was modulated

3. Experimental Procedure

A twenty-five milliliter sample of gasoline was taken and allowed to evaporate at ambient temperature (∿20°C). The effluent fractions were pumped off, trapped in a glass "U" tube at liquid nitrogen temperatures (Figure 39), and analyzed using the G.C.-A.A. detector with an 8 foot TCP column. An inverted funnel was placed over the sample container to insure that most of the effluent would pass through the collecting tube.

In a second study, gasoline was evaporated at 0°C, 20°C (room temp.), and 40°C. At various stages in each evaporation study, one microliter (1 μL) aliquots of the residual gasoline were analyzed for lead alkyls. Evaporation temperatures were controlled with water baths.

4. Results and Discussion

A sample of commercial gasoline was taken and allowed to evaporate. The fractions collected were (a) the

first two percent of gasoline to evaporate and (b) the cut between ten and fifteen percent evaporate. Gas chromatograms of the leaded gasoline and the quantity of lead determined in the evaporated fractions are shown in Figure 40.

It can clearly be seen that in the first two percent and in the fraction between ten and fifteen percent of evaporation, the amount of organic lead evaporated was extremely small. It can also be seen that the relative concentration of TML was significantly higher than the concentration of TEL evaporating from the gasoline. This is what would be predicted from partial vapor pressure data.

A sample of gasoline was taken from a fresh full tank of commercial gasoline and analyzed. After three days of normal use, a sample was again taken from the now partially filled tank. The gas chromatograms are shown in Figure 41.

The results showed an accumulation of TEL and MTEL in the gasoline. There was no appreciable decrease in the amount of TML in the gasoline. This data indicates that tetraethyl lead is preferentially retained in the gas tank during operation.

In the second evaporation study, TEL was observed to concentrate in the gasoline during evaporation. The two lighter lead alkyl components (TML and TMEL) concentrated until approximately 50% evaporation had occurred and then were evaporated (Figures 42 and 43). The heavier lead alkyls continued to concentrate to approximately

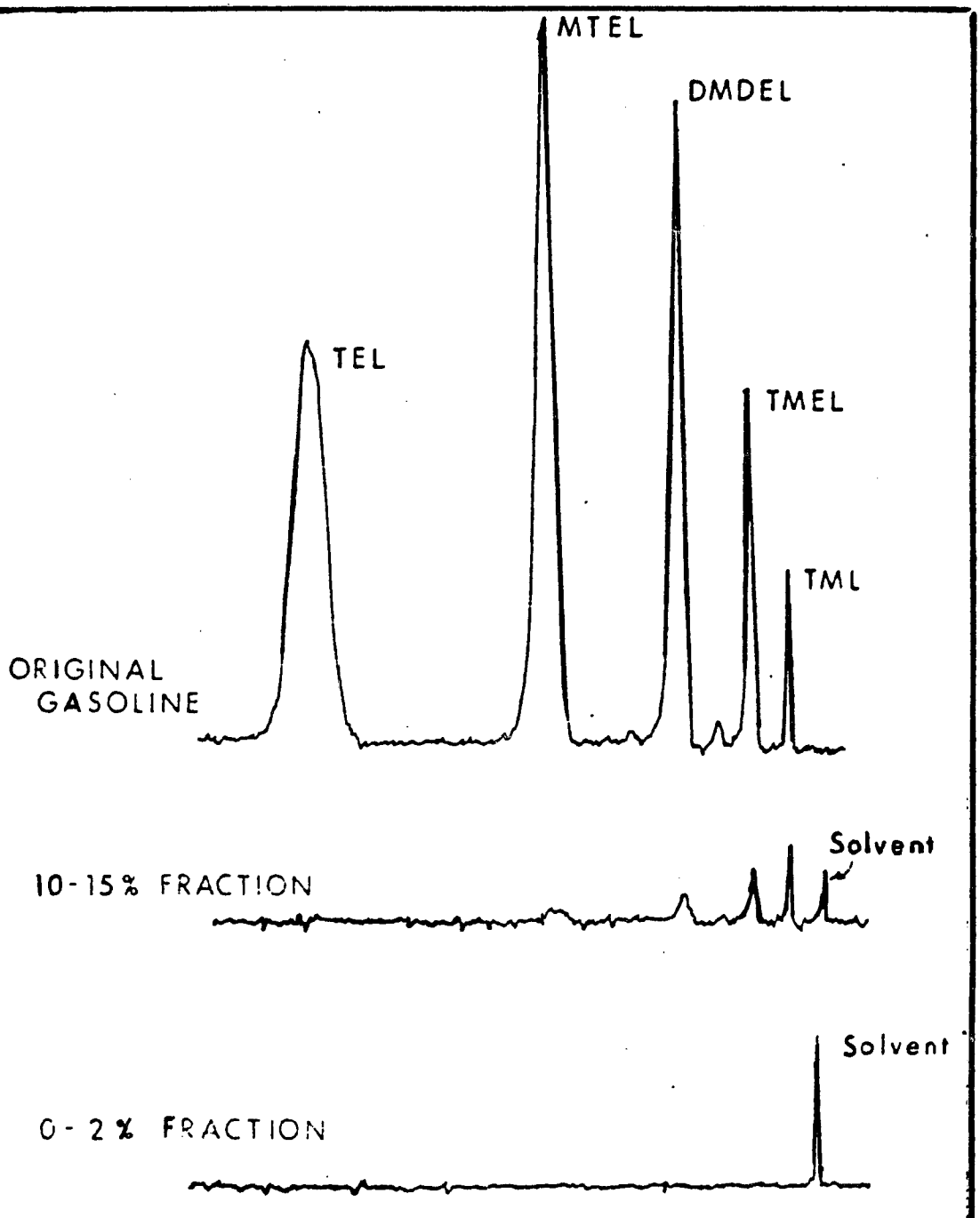


FIGURE 40:

Gas Chromatogram of Distillation Cuts of Gasoline Showing Low Lead Alkyl Concentration in Early Cuts.

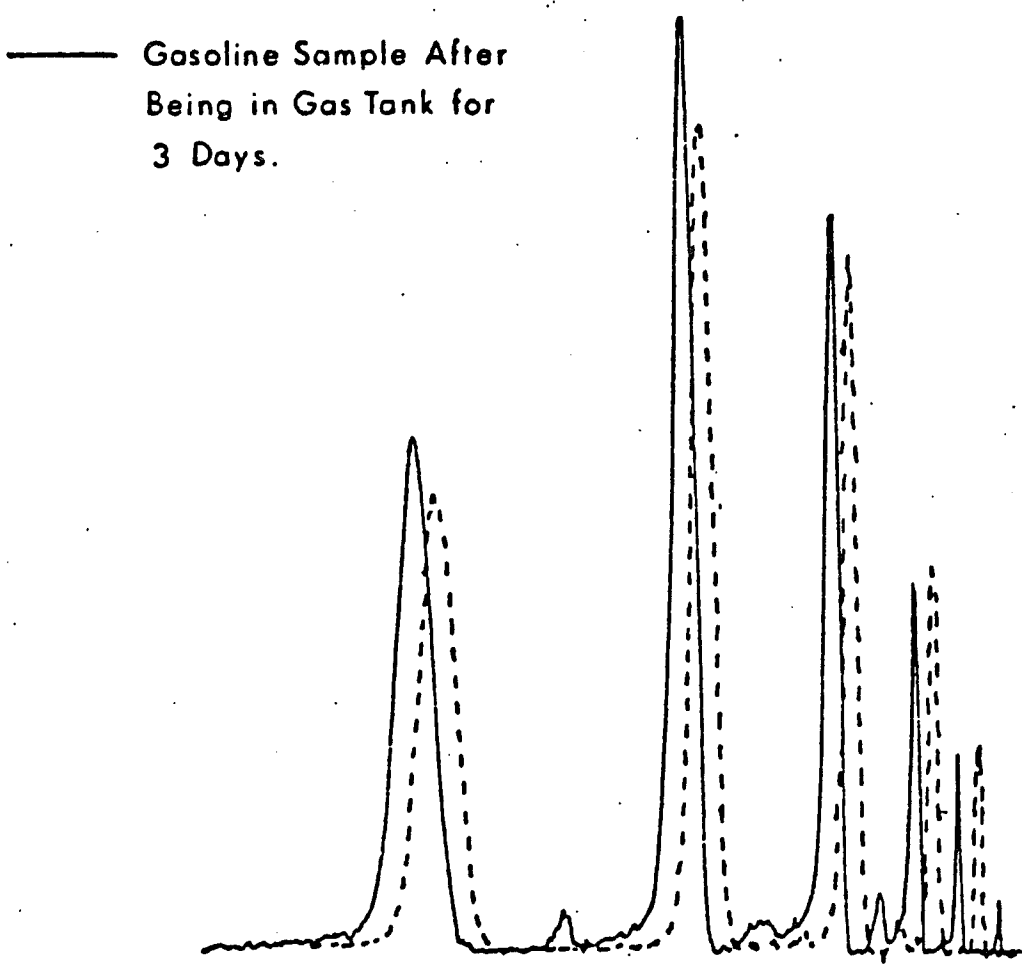


FIGURE 41:
Gas Chromatogram of ALKYL LEADS in AUTOMOBILE GAS TANK (slightly displaced for clarity)

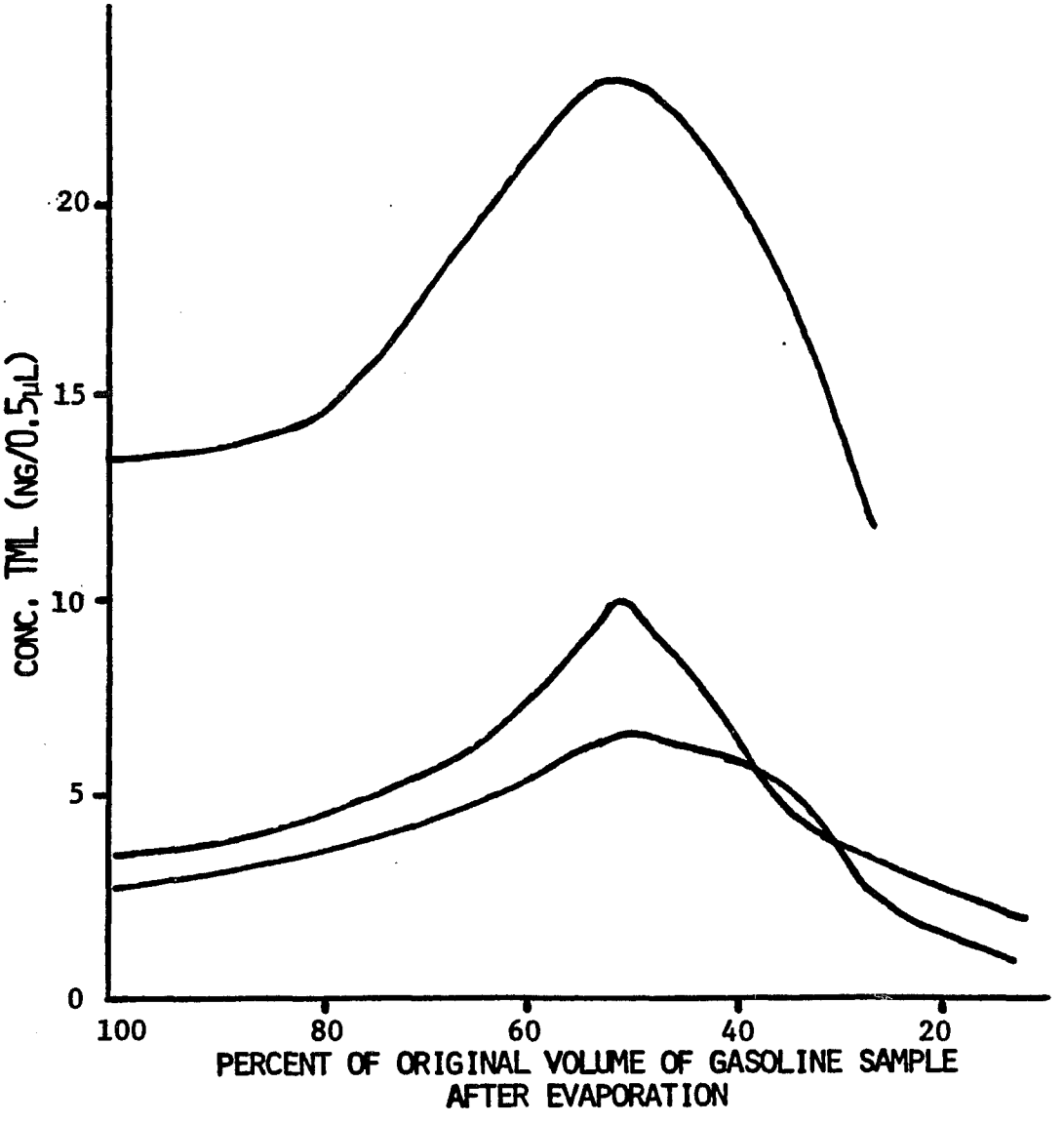


FIGURE 42: Concentration of TML in Gasoline vs. Percent Evaporation

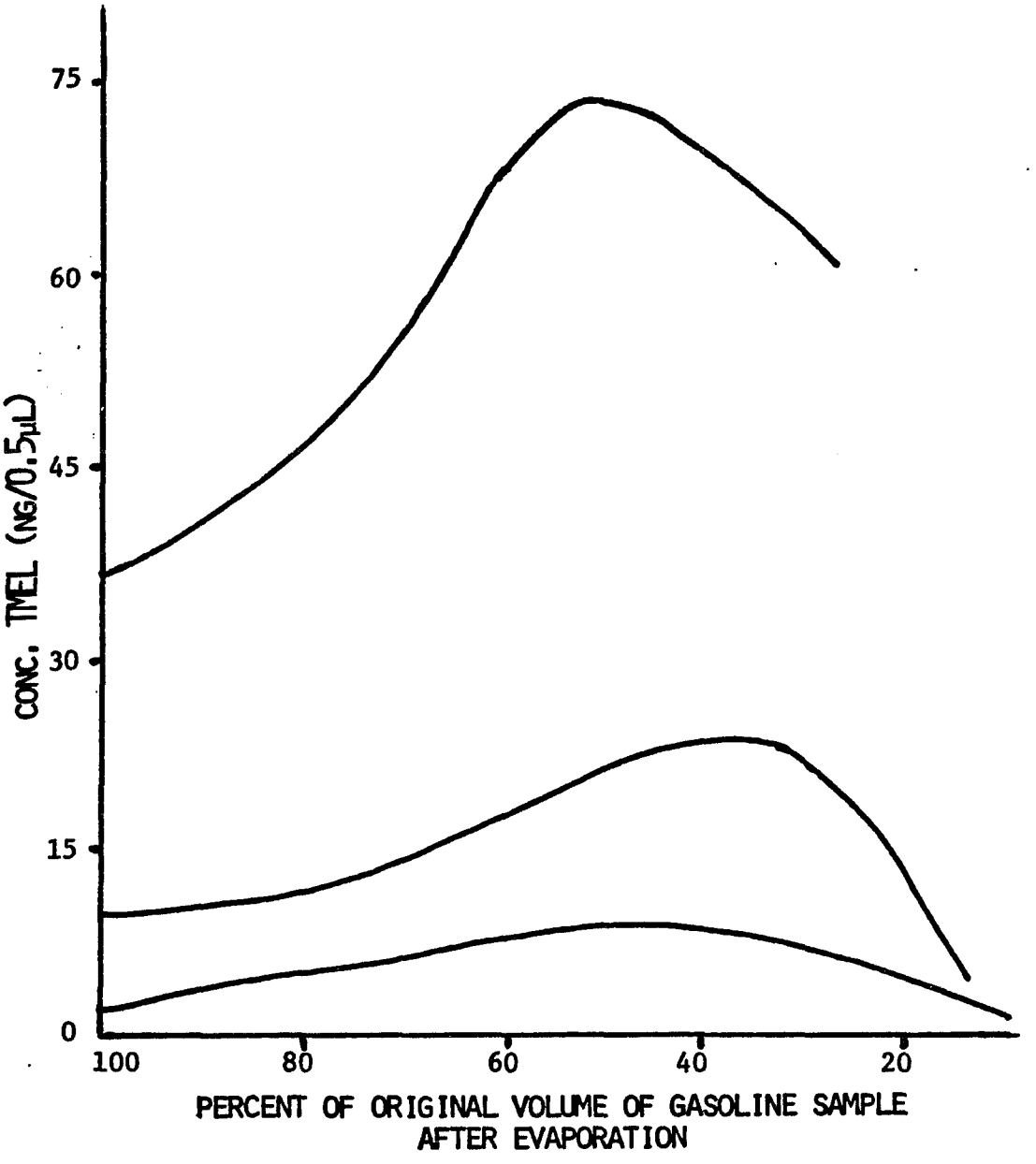


FIGURE 43: Concentration of TMEL in Gasoline vs. Percent Evaporation

90% evaporation.

These studies of the evaporate and the evaporation residue indicates that though some of the lead alkyls are lost to the atmosphere through the evaporation process, they tend to concentrate in the gasoline residue.

5. Summary

Simple evaporation of gasoline may lead to considerably lower quantities of lead in the atmosphere than have previously been believed. If only a small percentage of the gasoline evaporates, then this consists of very little leaded material.

When this data is viewed in conjunction with other data from this lab, it must be concluded that any procedure which uses a scrubbing agent designed to take out organic lead will have a major source of error and will give falsely low answers. These data also confirm the probability that "non-organic lead" (inorganic or atomic lead) is a significant proportion of the molecular lead detected in the atmosphere.

F. INTERACTIONS BETWEEN TETRAETHYL LEAD AND SEA WATER

1. Introduction

Tetraethyl lead has been used extensively as an antiknock agent in gasoline. Some lead alkyl compounds are more toxic than inorganic lead compounds.[85] There is a direct relationship between the liposolubility of a lead compound and its toxicity.[86]

Studies indicate that when tetraethyl lead (TEL) is introduced into a biological system, it is enzymatically converted in the liver to triethyl lead chloride (TrEL).[87,88] TrEL is approximately 100 times more toxic than TEL.[89,90,91] It has been proposed that TEL is non-toxic and that TrEL is the active compound in TEL toxicity[87,88] TrEL is soluble in water (<2 g/100 mL H_2O).[92] It is known to inhibit glucose metabolism and respiration in brain cells.[93] To evaluate the impact of TEL, it is important to determine if TEL is converted to TrEL in a given system.

Total lead determinations are not satisfactory because they give no indication of chemical form. Other methods that have been reported in literature to determine TEL, TrEL, and diethyl lead chloride (DiEL) involve elaborate, time consuming separation procedures which are subject to error. These methods include the use of the dithizone,[89] iodine monochloride,[94] or 4-(2-pyrydylazo)resorcinol (PAR).[95]

The major threat of lead pollution by lead alkyl compounds is from accidental spills. The first reported case of a major lead alkyl spill was in the Gulf of Trinidad in 1961. In 1962, a second spill was reported off Cape Town Harbour.[96] In 1974, the Yugoslav cargo ship Carta was lost 3.5 miles off Otranto Cape in the Adriatic Sea. She sank with 325 tons of lead alkyls aboard in 90 meters of water.[97]

Speculations of the environmental impact of the lead alkyls ranged from "no effect" to "will destroy the floor of the Mediterranean." Several important questions arose

concerning the dissipation of TEL through the sea water into the atmosphere, possible reaction products of TEL with sea water and their toxicities, etc. Studies were reported that dealt with the kinetics of TEL decomposition, its environmental half-life, and interactions with sea water and marine life.[90,97,99] TEL is known to produce TrEL in sea water as well as in blood. TrEL seems to be stable under experimental conditions.

The G.C.-A.A. system permitted the determination of both TEL and TrEL directly with no sample preparation of any kind. This study involves the apparent long term stability of TEL in sea water, the reaction rate of TEL with sea water, and the rate of loss of TEL when TEL is allowed to escape into the vapor phase.

2. Experimental Parameters

   a. Equipment

      1) G.C.-A.A. system (previously described)

      2) Reaction vessel with a specially designed teflon valve (Figure 44)

   b. G.C. Operating Conditions

      1) Column - 1/8 inch diameter teflon column, 8 inches long, packed with 20% Ucon Non-Polar on Chromosorb P (Microtek, Inc.)

      2) Carrier Gas - Argon (∿60 cc/min)

      3) Column temperature - 90°C

      4) Injection port temperature - 115°C

      5) Transfer line temperature - 110°C

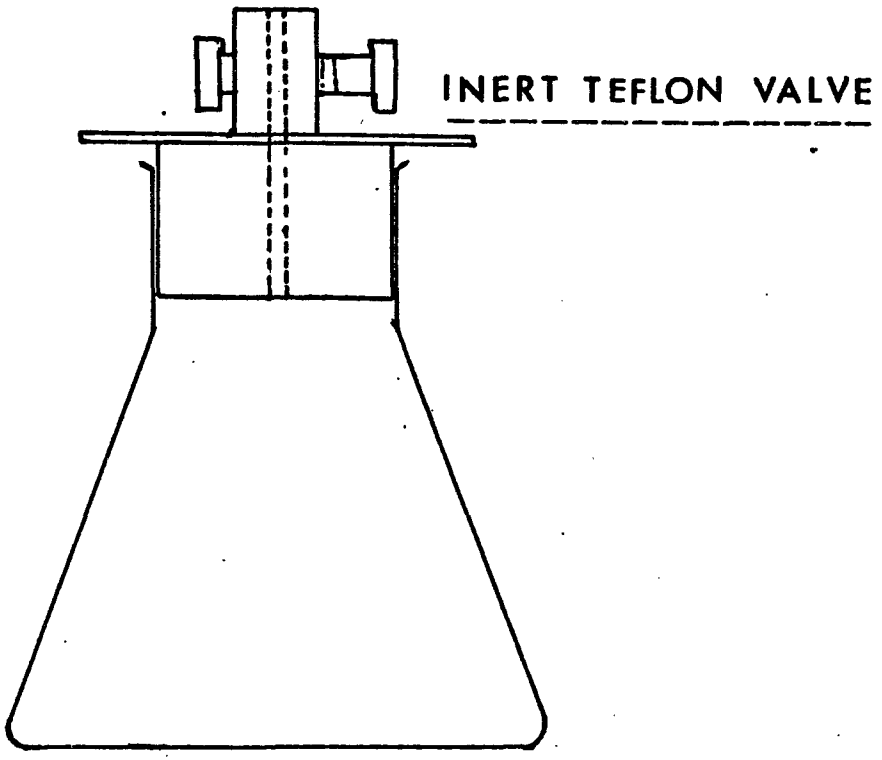


FIGURE 44: Schematic diagram of reaction vessel with specially designed Teflon valve.

c. A.A. Operating Conditions

1) Lamp current - 35 mA

2) High voltage on P.M. tube - 400 V.D.C.

3) Slit Width - 25 microns

4) Atomizer Temperature - 1600°C

d. Chemicals

1) Sea water - collected from different places in the Gulf of Mexico

2) TEL

3) Heptane

4) Artificial Sea Water

- Deoxygenated deionized water (1 liter)
- Na^{+} as NaCl 0.456 mmoles/L
- Mg^{++} as $MgCl_2$, $MgSO_4$ 0.054 mmoles/L
- K^{+} as KCl 0.01 mmoles/L
- Ca^{++} as $CaCl_2$ 0.01 mmoles/L
- Cl^{-} as NaCl, $MgCl_2$, KCl, $CaCl_2$ 0.543 mmoles/L
- $SO_4^{=}$ as $MgSO_4$ 0.028 mmoles/L

3. Experimental Procedure

a. Stability and solubility study

A 25 µL aliquots of TEL was placed in 100 mL of sea water in a glass container. The container was covered with aluminum foil to exclude light. The mixture was sampled and monitored periodically on the G.C.-A.A. to determine the long term effects in stationary, light-tight systems.

b. Vapor Study

A 25 mL sample of sea water was placed in a 50 mL Erlenmeyer flask and 200 µL of TEL were added. The flask was stoppered with a specially designed teflon valve to prevent air leaks, and was covered with aluminum foil in order to exclude light. 1 mL samples of vapor over the liquid were run in the G.C.-A.A. and compared with 1 µL aliquots of standards of TEL in heptane.

c. Interaction Between TEL and Sea Water

Samples composed of artificial and natural sea water were placed in small bottles. The specially designed valves were used to stopper the small bottles holding about 33 mL filled to the top to eliminate any interaction with a vapor phase. 200 µL of TEL was added to approximately 33 mL of sea water. These samples were shaken thoroughly and allowed to settle for at least 2 months. A typical G.C.-A.A. trace is shown in Figure 45. These samples were periodically checked using the G.C.-A.A. system and G.C.-M.S. in order to determine the identity of the second unknown peak.

4. Results and Discussion

a. Long Term Solubility and Stability of TEL in Sea Water

Samples were periodically analyzed for TEL. These were light excluded, undisturbed samples with an excess of TEL at the bottom of the containers. After about 200 days, TEL was still present in a separate phase

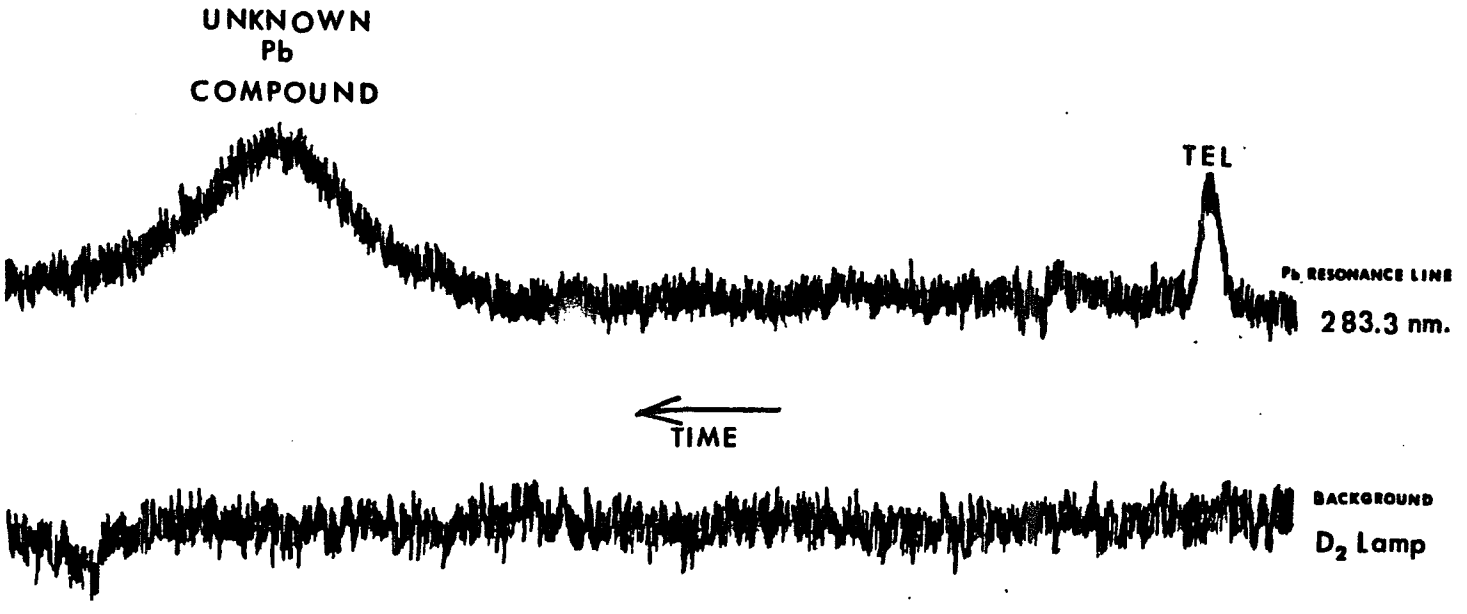


FIGURE 45: G.C. trace of TEL and unknown lead compound in natural sea water spiked with TEL.

at the bottom of the container. Concentrations of the TEL and the unknown lead compound, which was later identified as TrEL are shown in Figure 46. These values were somewhat scattered due to traces of TEL emulsion. It is clearly indicated that TEL did not convert to less harmful inorganic lead compounds in a short period of time. With excess TEL, its solubility may slowly increase with time with simultaneous formation and accumulation of the more stable TrEL. Because there was an excess of TEL in a separate phase, any TEL that converted to TrEL was quickly replaced and a dynamic system was established.

It was observedthat a grayish substance (possibly an emulsion) coated the surface of the TEL droplets on the bottom of the container. The effect of the surface coating on the stability and reactivity of TEL was unknown. A similar coating of TEL had been observed in biological growth medium that TEL had been added to.[100]

b. Vapor Study

The concentration of TEL in the gas phase above the TEL-sea water mixture was approximately 430 μg of Pb as TEL per mL of gas. This was an unexpectedly high concentration. This study indicated that TEL diffused very rapidly through sea water into the vapor space. In an open system, this may provide a mechanism for TEL to leave sea water and enter the atmosphere within a short time. Once in the atmosphere, TEL can photodecompose or be adsorbed onto airborne particular matter.[101-103]

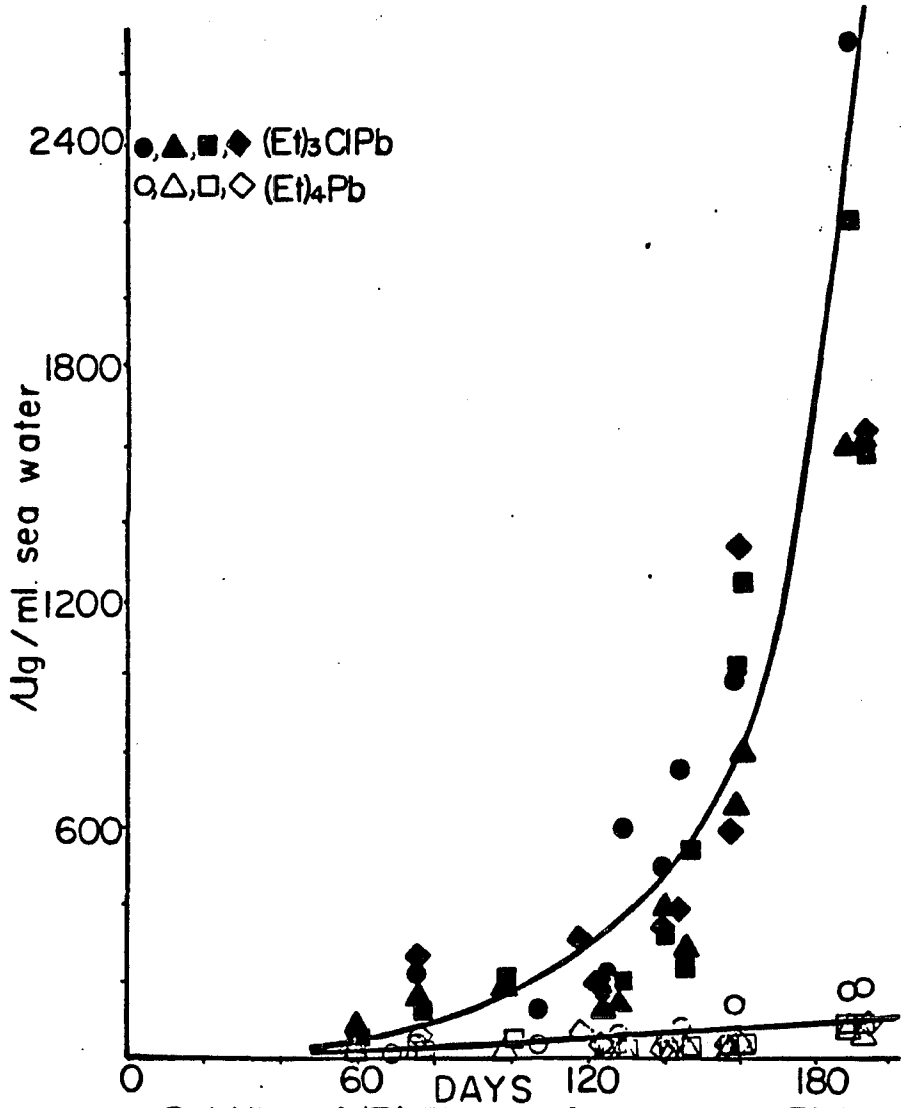


FIGURE 46: Solubility of $(Et)_4Pb$ and formation of $(Et)_3ClPb$ in sea water with respect to time.
○ ● artificial sea water, deoxygenated.
△ ▲ sea water, filtered.
□ ■ sea water, filtered.
◇ ◆ sea water, deoxygenated.

c. Interaction between TEL and Sea Water

Two volatile lead containing compounds were present in sea water after TEL was added to it. One compound was identified as TEL by comparison of G.C. retention times. TEL forms a nonhomogeneous mixture with sea water. Studies indicated that there was an initial decrease in the TEL concentration. The concentration of a second volatile lead compound tended to increase with time. Attempts to identify the unknown lead compound by G.C.-M.S. were unsuccessful. Later the column conditions which had been optimized for TEL determinations were altered. The column temperature was raised to 140°C, the inlet and transfer line temperatures were raised to 150°C. A typical G.C.-A.A. trace is seen in Figure 47. G.C.-M.S. studies indicated that the second peak was triethyl lead chloride (TrEL) (Figures 48 and 49). Elution through a G.C. column indicated that TrEL was volatile at higher temperatures.

5. Summary

The results suggest that TEL lies at the bottom of a sea bed in a separate liquid phase and only slowly dissolves into the sea water. TEL appears to be stable in this environment for long periods of time. TEL tends to migrate rapidly to the surface and evaporate into the atmosphere. TEL reacts steadily with sea water to form TrEL which is water soluble and accumulates steadily in the water.

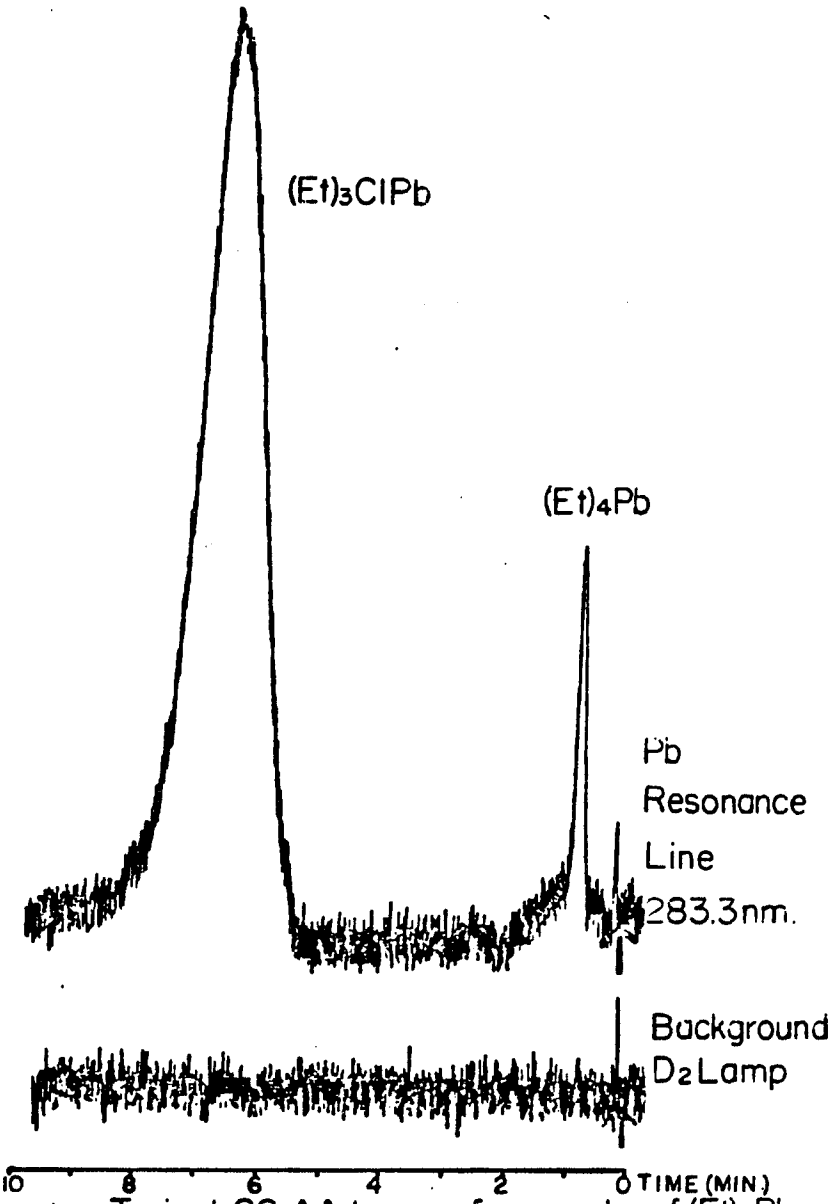


FIGURE 47: Typical GC-AA trace of a sample of $(Et)_4Pb$ in sea water.

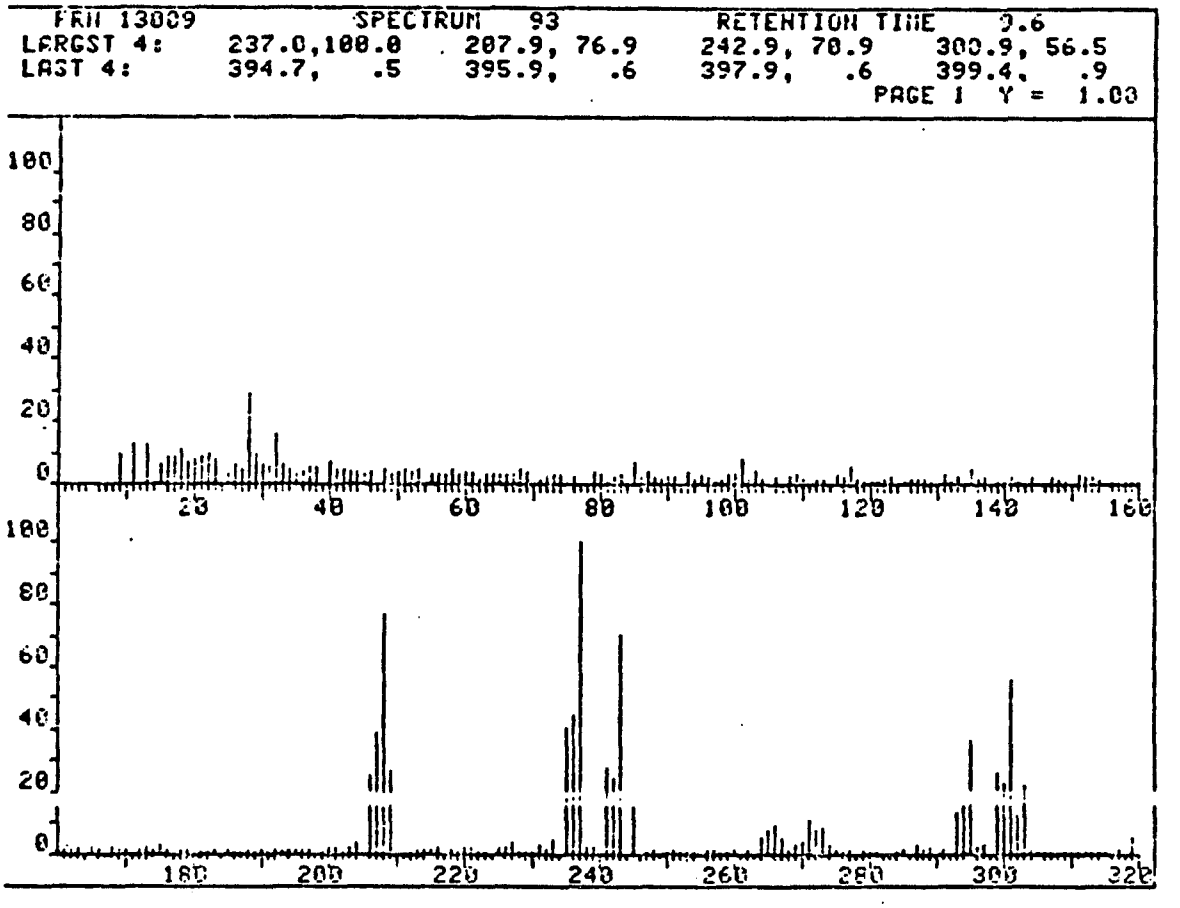


FIGURE 48: MS of the second peak observed in the GC-AA trace of a sample of $(Et)_4Pb$ in sea water & $(Et)_3ClPb$.

MASS	ABUND	
190	.9	
190	1.0	
191	1.3	
192	.8	
194	1.0	
195	.9	
196	1.7	
197	1.1	
199	.4	
200	3.6	
202	.9	
203	2.7	
204	4.2	
206	25.5	Pb_{206}
207	35.2	Pb_{207}
208	78.8	Pb_{208}
209	30.7	
210	1.2	
211	.8	
212	1.6	
213	.6	
214	1.6	
216	.6	
217	3.2	
218	1.8	

MASS	ABUND	
219	2.4	
220	2.2	
221	1.3	
222	1.0	
222	1.2	
223	.8	
224	.6	
225	2.4	
227	1.9	
228	.9	
229	.6	
230	1.1	
231	1.7	
232	1.0	
233	4.7	
234	.8	
235	41.7	
236	46.0	
237	100.0	PbEt
238	2.4	
239	1.0	
241	27.0	
242	25.0	
243	63.3	$PbCl_{35}$
244	9.5	

MASS	ABUND	
245	21.2	$PbCl_{37}$
246	1.1	
247	1.1	
248	.7	
249	.5	
250	.6	
250	.6	
251	.7	
251	1.2	
253	.9	
254	1.0	
254	.7	
255	1.1	
256	.8	
257	1.1	
259	1.6	
260	1.1	
261	.9	
261	.8	
263	1.6	
264	8.1	
265	8.8	
266	10.7	$Pb(Et)_2$
269	2.8	
270	2.9	
271	8.3	

MASS	ABUND	
272	9.0	$PbCl_2Et$
273	7.7	
274	4.8	$PbCl_3Et$
275	1.4	
275	.9	
276	.9	
277	.9	
278	.8	
279	1.3	
280	.4	
281	.8	
282	.6	
282	1.3	
283	.6	
284	.8	
284	.9	
285	1.1	
286	1.1	
287	2.0	
288	2.8	
289	1.3	
291	1.7	
292	.5	
293	14.7	
294	13.6	
295	32.6	$Pb(Et)_3$

MASS	ABUND	
296	2.1	
297	2.2	
299	24.4	
300	29.6	
301	61.4	$PbCl_2(Et)_2$
302	10.3	
303	16.4	$PbCl_3(Et)_2$
304	1.4	
305	.4	
306	.5	
308	.4	
309	1.0	
310	.6	
311	.6	
311	.4	
311	.5	
313	1.3	
315	.6	
315	.7	
316	.6	
317	.6	
319	5.4	
320	6.3	
321	9.9	
322	1.1	

MASS	ABUND
323	.5
324	1.0
325	.6
326	.6
327	.4
328	1.4
329	1.4
330	2.5
331	1.5
332	.6
332	.7
333	.9
333	.7
335	.8
336	.4
337	.7
338	.4
339	.6
341	.5
342	.4
343	1.5
344	.6
345	2.7
347	1.3
348	1.0

FIGURE 49: MS tabulation of $(Et)_3ClPb$.

The solubility of TEL in sea water was not found to be very dependent upon the type of water. The solubility increased with time and at rates that were dependent upon the experimental conditions.

The G.C.-A.A. provided a method of analysis that was simple, rapid, and allowed direct separation and determination of TEL and TrEL without pretreatment of the samples. This was a valuable improvement over existing methods of analysis for these compounds which involve time consuming wet chemical procedures.

Later studies (not reported here) of TEL and TrEL in sea water without an excess of TEL present indicated an equilibrium between these compounds with a predominance of TrEL. There was evidence of a loss or further reaction of TrEL with time, but this was not studied.[41,104]

G. METHYLATION OF CADMIUM WITH VITAMIN B_{12}: A POSSIBLE METHOD OF DETOXIFICATION

1. Introduction

Cadmium compounds are toxic. Very low concentrations can have adverse health effects.[1,105] Cadmium (Cd) is known to be a cumulative toxin. It tends to concentrate in the kidneys and the liver.[106] The estimated human biological half-life is between 9 and 30 years.[105] Recent data indicates that the actual biological half-life may be considerably less (ca. 1-2 years).[107] Poisoning by cadmium can be acute or chronic. It causes a variety of systemic manifestations including nasopharyngeal irritation,

chest constriction, cough, dyspnea, and delayed onset of pulmonary edema.[108,109] Cadmium has also been related to renal dysfunction,[17-19] anemia,[23] and hepatic dysfunction.[16]

It has been proposed that exposure to cadmium may be a major factor in the pathogenesis of essential hypertension.[110] Studies have indicated that renal cadmium concentrations were significantly higher in patients with hypertension than in normal subjects.[1,111] Hypertension has been induced in experimental animals by adding Cd to their drinking water[112] or to their diet.[113,114-116] The mechanism of Cd-induced hypertension is not clearly understood. It has been suggested that it is associated with renal dysfunction and the subsequent fluid and electrolyte imbalance.[110,117,118]

For many years it has been known that Cd can cause tumors in experimental animals.[119,120] Recently Cd exposure has been correlated to an increased rate of human prostatic cancer.[121] Because of this, Cd has been included on NIOSH's list of suspected carcinogens[122] and on IARC's list of possible cancer risks.[123]

Cadmium has been shown to interfere with various metabolic processes.[124,127] It is believed to bind to many enzymes and inhibit their activity.[110,126-128] Cadmium is thought to displace zinc in several enzymes and thus induce diseases through renal or hepatic zinc deficiences.[111,129,130] Zinc is a coenzyme of at least eighty metabolic enzymes.[131]

There is no good indicator for the severity of Cd exposure. Symptoms and Cd concentrations in urinary excretions bear no relationship to the severity or duration of exposure. At best by monitoring such things, only a confirmation of absorption can be made.[108] The actual excretion of Cd from the body is very slow and concentrations appear to be higher in feces than in urine.[132]

The rate of excretion of cadmium through sweat is higher than through other routes of excretion. A recent study indicates that a person not occupationally exposed to cadmium will excrete daily about an equivalent amount of cadmium to the average daily intake.[107]

It has been suggested that the cadmium to zinc ratio in the body may be a more meaningful measure of the effect of Cd exposure. Because of the exchangeability of the metals, in some cases zinc can prevent certain Cd induced symptoms[1,133-139]

2. Human Exposure to Cadmium

Cadmium is widely dispersed in our environment. It is present in trace quantities in air, water, and food.[1,105,140] Food and water consumption have been considered to account for the majority of daily Cd intake.[1,136]

Normal concentrations of Cd in food are less than 0.05 ppm. Daily dietary intake is about 50 µg.[105] Drinking water contains less than 1 ppb. Higher concentrations have been reported in industrial areas.[105,141] Normal levels in

the air are approximately 0.01 to 0.05 μg/m^3 of air.

Smokers, however, are exposed to significantly higher concentrations (ca. 1.0 - 1.5 μg Cd/cigarette).[138,139,142] This is equivalent to an exposure of 4.5 μg/m^3 in cigarette smoke. It has been estimated that between 25 and 50 percent of the Cd inhaled is absorbed by lung tissue.[1,110] This Cd exposure has a direct correlation to hypertension and cardiovascular disease.[1]

3. Detoxification with Vitamin B_{12}

A common method of detoxification of chemicals and heavy metals in the body is via methylation. Several compounds are believed to be methylated in the liver and then removed from the body during respiration. Vitamin B_{12} is known to be a natural methylating agent which is involved with metabolic methylations.[143,144] Several heavy metals have been shown to be methylated by microorganisms.[145,146] Recent interest in heavy metal poisoning has shown that methylated Vitamin B_{12} (MeB_{12}) can non-enzymatically methylate heavy metals.[145,147-152] Among the metals that can be methylated with Vitamin B_{12} are Hg (II), Tl (III), Pd (II), Cr (II), Pt (II)•(IV), Au (I)•(III) and Cu (II). Because these metal alkyls are volatile, methylation becomes a possible method of detoxification. Many of these studies have demonstrated the methylation of heavy metals with MeB_{12}, but most have not been carried out at physiological pH (7.4). This is significant in that most of these reaction equilibriums will be changed with varying pH.

4. Experimental Parameters

a. Equipment

1) Reaction apparatus (Figure 50)

2) "Quartz T" Atomic Absorption unit (Figure 51)

3) G.C.-A.A.

b. Atomic Absorption Parameters

1) Lamp current - 30 mA

2) High voltage to PM tube - 500 V.D.C.

3) Slit width - 100 microns

4) Analytical Wavelength - 228.8nm

5) Background Correction Wavelength - 226.5nm

6) Atomizer Temperature - 1350°C

c. Chemicals

1) Vitamin B_{12} - Sigma Co.

2) $NaBH_4$ - Fisher Scientific Co.

3) $Co(NO_3)_2$ - Allied Chemical

4) CH_3I - J.T. Baker Chemical Co.

5) $NaHCO_3$ - J.T. Baker Chemical Co.

6) $CdCl_2$ - J.T. Baker Chemical Co.

7) Argon

5. Experimental Procedure

a. Methylation of Vitamin B_{12}

The methylation of Vitamin B_{12} (Cyanocobalamin) was carried out under an inert argon atmosphere following the procedure outlined by D. Dolphin.[153] The B_{12} solution (100 mg in 10 mL H_2O + 1 mg $Co(NO_3)_2$ was reduced with

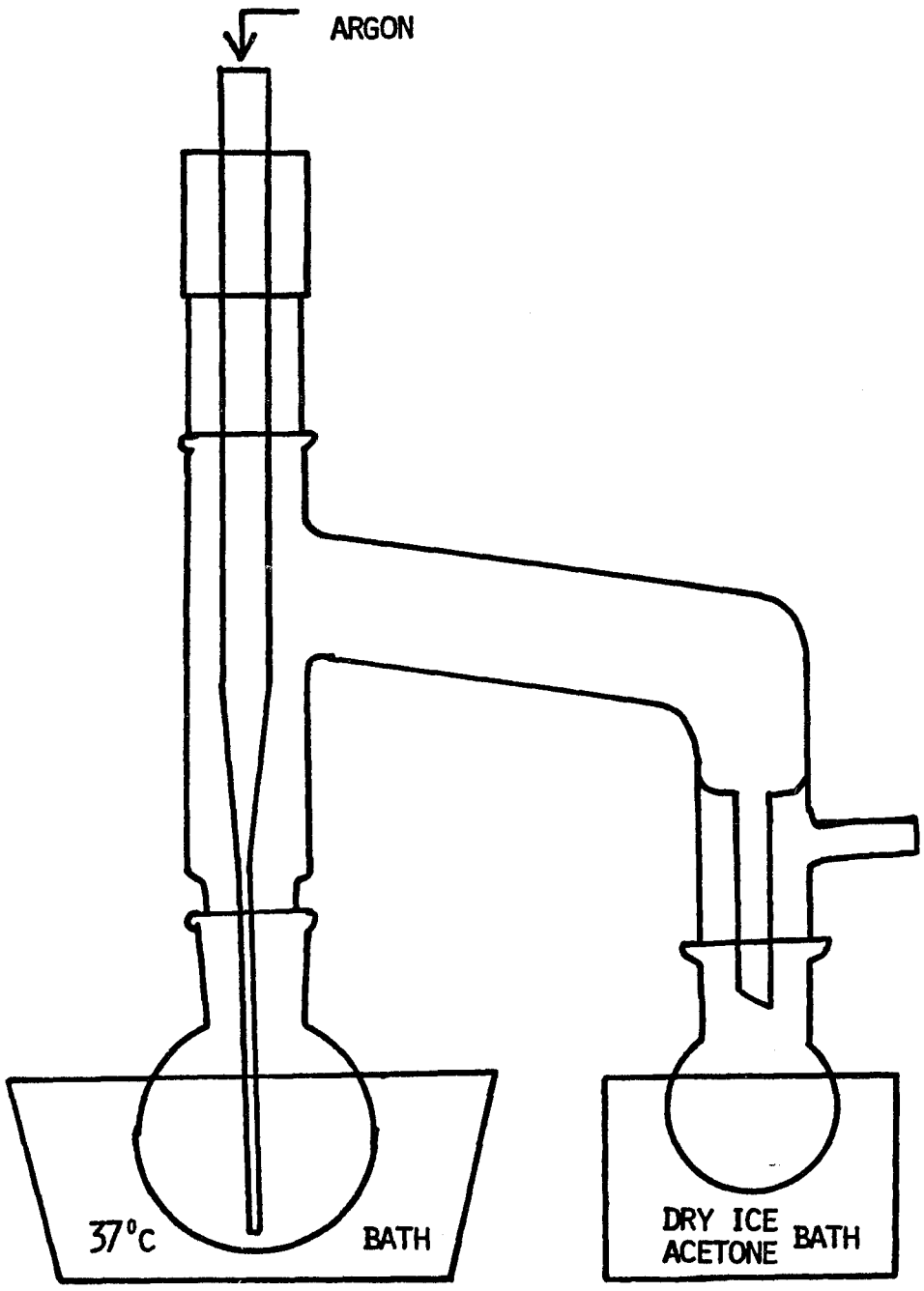


FIGURE 50: Reaction Apparatus for MeB_{12} and $CdCl_2$

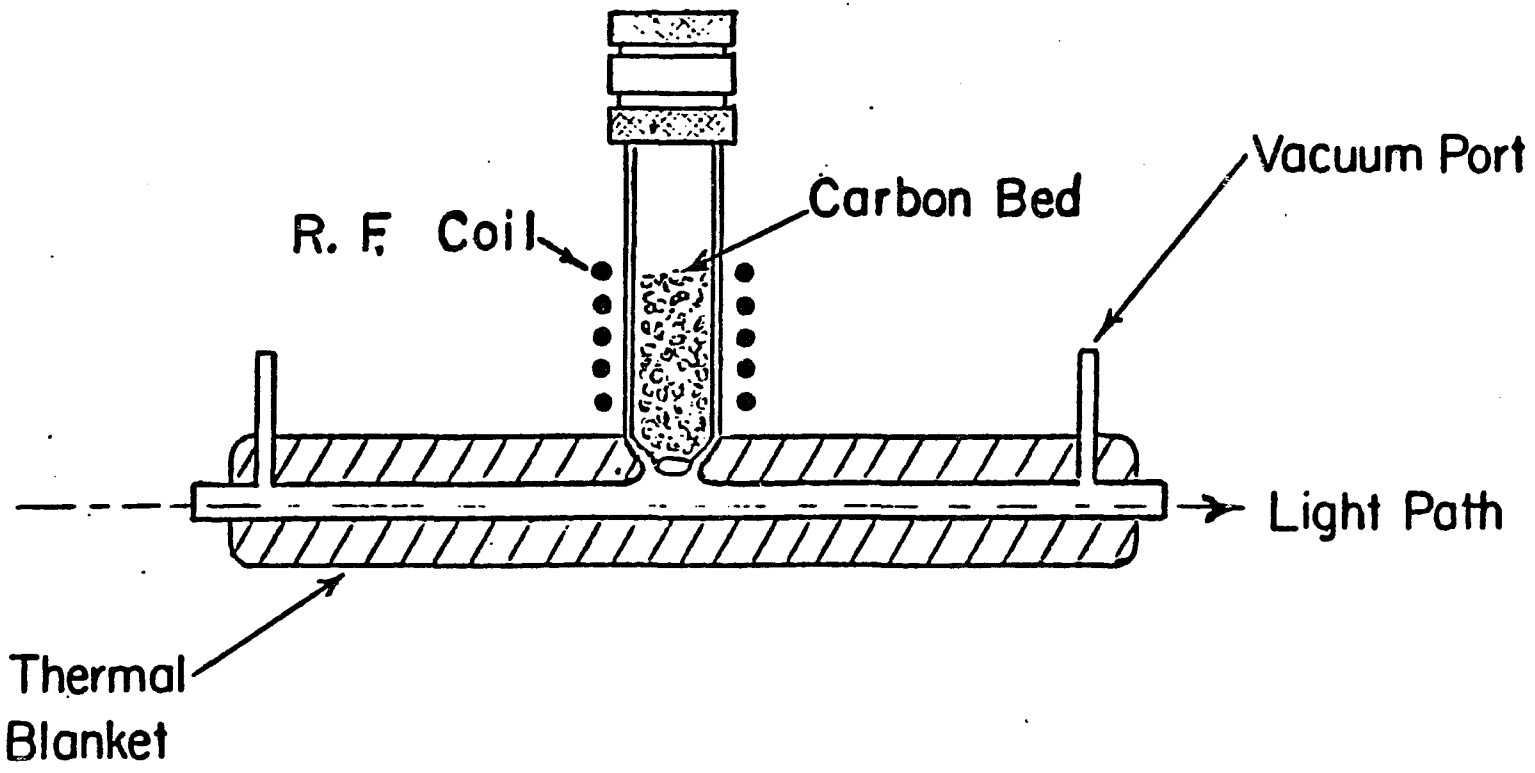


FIGURE 51: Schematic diagram of the Quartz "T" Carbon Atomizer.

sodium borohydride (20 mg $NaBH_4$ in 0.5 mL H_2O). The reaction immediately turned dark. It was then allowed to stand for 5 minutes. Methyl iodide (200 mg CH_3I, ca. 0.1 mL) was then added to complete the methylation reaction. This resulted in a mixture of methylated Vitamin B_{12} (MeB_{12}) and aquocobalamin with traces of $Co(NO_3)_2$ and CH_3I.

A similar reaction was set-up and simultaneously run as a blank. In the blank only Vitamin B_{12} was not added. A solution (1 mg $Co(NO_3)_2$ in 10 mL H_2O) was reduced with sodium borohydride (20 mg $NaBH_4$ in 0.5 mL H_2O). The reaction was allowed to stand for 5 minutes. Methyl iodide (200 mg CH_3I, ca. 0.1 mL) was added to complete the methylation reaction.

Argon was allowed to bubble through the reaction vessels throughout the entire experiment at a rate of 20 mL/min. The methylated reaction mixtures were allowed to stand 1 hour to remove the excess methyliodide.

b. The Reaction of Vitamin Methyl B_{12} and Cadmium Chloride

The pH of a saturated solution of cadmium chloride ($CdCl_2$) was adjusted with sodium bicarbonate ($NaHCO_3$) to pH 7.4. It was added in a 1:1 volume ratio to the above mixture.

The collection vessel was then added to the apparatus and was cooled in a dry ice-acetone bath. The reaction vessel was heated to 37°C. The reaction was allowed to run 9-10 hours.

Any volatile compounds formed in the reaction were analyzed for total cadmium using atomic absorption.

6. Results and Discussion

With the distillation apparatus used, only volatile compounds could be collected in the receiving vessel (Figure 50). The reaction vessel was heated to 37°C which is the normal human body temperature. Argon was continuously bubbled through the medium to insure an inert atmosphere and to act as a mobile phase to assist in the transport of any volatile compounds that may be generated in the reaction vessel. Total cadmium was analyzed on the "quartz T" atomizer.

Cadmium was found in the collection vessels. On two separate occasions aqueous solutions, 50 µL and 45 µL respectively, were found. The first solution had a concentration of 43±10 ppb Cd. The total cadmium content was approximately 2×10^{-9} g Cd. The concentration of the second solution was 20±3 ppb Cd. The total amount present was approximately 9×10^{-10} g Cd. This indicated that a volatile Cd compound was formed in the presence of MeB_{12}. Mass spectroscopy was attempted on the solutions without success. The concentrations were below the practical detection limits of the instrument.

The pH of the solutions were tested and found to be 9.6. This was initially assumed to be due to the $NaBH_4$ which was added to reduce the B_{12}. It was then determined that the pH of the saturated $CdCl_2$ solution had increased

to 9.6. The pH of the saturated $CdCl_2$ solution was adjusted again to a pH of 7.4.

The reactions were run again and the pH was checked and confirmed to be 7.4. After 9.5 hours the distillate was analyzed for total Cd. The Cd level in the blank and in the sample were the same. It was concluded from this study that MeB_{12} did not form a volatile compound with cadmium at pH 7.4.

Attempts were made to utilize the G.C.-A.A. in a speciation study. Dimethyl cadmium was synthesized via a Grignard reaction. It was assumed that only dimethyl cadmium would be present in an organic solvent, so the solution was analyzed for total Cd. Dilutions of this solution were used to calibrate the G.C.-A.A.

Dimethyl cadmium was found to be very reactive and relatively unstable. It tended to decompose in the instrument. Reliable results could not be obtained using the G.C.-A.A. in its present form, so this technique was abandoned.

The importance of the reaction between MeB_{12} and Cd to form a volatile Cd compound is that it may be a possible mechanism of detoxification in cases of Cd poisoning. The reaction appeared to favor the higher pH of 9.6. This is of interest because this is also the pH at which Cd replaces Zn in enzymes.[154]

7. Summary

A volatile cadmium compound was formed in the reaction of Vitamin methyl B_{12} with $CdCl_2$ at a pH of 9.6. This reaction is a possible mechanism of detoxification through respiration in cases of cadmium exposure, although the concentration at which the volatile cadmium compound is formed is very low and pharmacologically impractical.

The G.C.-A.A. was not used in this analysis because proper chromatographic conditions could not be obtained to perform an analysis that was sensitive enough. Similarly, the compound or compounds could not be identified by mass spectroscopy because the entire sample size was smaller than the detection limits of the instrument.

CHAPTER 4

CONCLUSION

A. SUMMARY OF RESULTS

A new atomic absorption detector for gas chromatography was developed. The detector was a modified, reduced "hollow T" carbon atomizer. The carbon "T" was electrothermally heated to atomization temperature. The atomization process occurred in the base of the "T" and then free atoms were swept into the crosspiece or light path where optical measurements were taken. The atomic absorption detector was directly interfaced to a gas chromatograph through a pyrex transfer line. The detector exhibited the excellent specificity of atomic absorption while retaining the sensitivity of carbon furnace atomizers. The separation capability of gas chromatography allowed the atomic absorption detector to be used selectively for different chemical forms of a given element.

1. Determination of Lead Alkyls in Gasoline

The determination of lead alkyls in gasoline was chosen as a practical sample to demonstrate the gas chromatography-atomic absorption system (G.C.-A.A.) as an important analytical technique for characterizing mixtures

containing volatile metal compounds. Molecular background interference was determined using a deuterium lamp and was found to be negligible.

2. Sensitivity of the Gas Chromatography-Atomic Absorption System

The sensitivity of the "hollow T" G.C.-A.A. was approximately 30 times greater than a similar G.C.-A.A. with a flame atomizer as the detector. The G.C.-A.A. system was modified by replacing the stainless steel column and transfer line with a less reactive glass transfer line and a teflon column. Because less sample decomposition occurred in the instrument, the sensitivity was improved to approximately 450 times greater (ca. 10^{-10} g Pb per 1 µL sample size) than the flame atomizer-G.C. combination.

3. Determination of Lead Compounds in Unleaded Gasolines

Unleaded gasoline samples were studied. When low-lead and unleaded gasolines were first introduced, traces of lead compounds were found in them (these were within the government's allowable levels). This was probably due to traces of lead alkyls from the leaded gasolines that previously occupied the storage tanks at the gas stations. After several months, lead compounds were no longer detected in unleaded gasolines. It was presumed that the traces of lead originally observed had been effectively scavenged from the storage tanks by the unleaded gasolines or converted to non-volatile

lead species.

Molecular absorption was noted and assumed to be caused by the functional groups of organic compounds that have broad band absorption in the region of the lead 283.3 nm line.

It was found that the molecular absorption of these compounds was very dependent on temperature. As the atomization temperature increased, the molecular absorption increased correspondingly, indicating that the actual absorbing species was a combustion product and not undecomposed compounds.

4. The Gas Chromatography-Atomic Absorption System as a Nonspecific Detector

The G.C.-A.A. system was then utilized as a nonspecific detector. Organic compounds with various functional groups were analyzed. It was found that alkyl and aromatic halides, amines, and thiols absorb the lead 283.3 nm line. Except for the aromatic halogen compound, the G.C.-A.A. lacks the sensitivity to be routinely used as a nonspecific detector.

5. A New Modified Atomic Absorption Detector

A new modified atomic absorption detector was designed and built for the G.C.-A.A. The purpose of the new design was to improve the lifetime of the resistance heated carbon element and thus prolong its usefulness.

Several designs for the carbon element were studied. It was determined that though the volume of the atom-

ization chamber was not critical, it could be too large. Atomization efficiency was improved when the atomization chamber tapered before entering the light path and when the light path was lengthened and maintained at atomization temperature.

The optimum flow rate for the G.C.-A.A. was determined from both a van Deemter plot and an atomization efficiency (peak area) versus flow rate plot. The two were not necessarily the same. Both had to be used to optimize the system.

6. Evaporation of Lead Alkyls from Gasoline

The evaporate of gasoline and the gasoline residue were studied at various stages during the evaporation process. Simple evaporation of gasoline may lead to considerably lower quantities of lead in the atmosphere than have previously been believed. Gasoline components tended to evaporate preferentially according to their vapor pressures. If only a small percentage of gasoline evaporated, then this consisted of very little leaded material. The lead alkyls tended to concentrate in the gasoline residue.

7. Tetraethyl Lead in Sea Water

Tetraethyl lead (TEL) in sea water was studied. TEL appears to be stable in sea water for long periods of time. It tends to remain in a separate liquid phase on the bottom. TEL will tend to migrate rapidly to the surface and escape into the atmosphere. Some of the TEL will react

with the components of sea water to form triethyl lead chloride (TrEL).

The G.C.-A.A. provided a method of analysis that was simple, rapid, and allowed direct separation and determination of TEL and TrEL. No sample preparation was required. This was a considerable improvement over existing methods of analysis for these compounds which involve time consuming chemical procedures.

8. Methylation of Cadmium By Vitamin Methyl B_{12}

Cadmium is a cumulative toxin. It exhibits both acute and chronic poisoning with a variety of adverse systemic effects. The major health effects of cadmium toxicity are renal dysfunction, hypertension, and cardiovascular disease. Cadmium (Cd) has also been implicated as a possible carcinogen.

Methylation is a common method of detoxification in biological systems. Vitamin methyl B_{12} (MeB_{12}) is a natural methylating agent. It has been shown that many heavy metals can non-enzymatically be methylated by MeB_{12}.

A volatile cadmium compound was formed in the reaction of MeB_{12} with $CdCl_2$ at a pH 9.6 in vitro. It has been suggested that this is the pH at which Cd replaces Zn in enzymes. This reaction is a possible mechanism of detoxification through respiration in cases of Cd exposure. The concentrations formed, however were very low and probably pharmacologically impractical.

The G.C.-A.A. system developed during this dissertation research is very sensitive and selective. It is ideal for speciation studies involving volatile metal compounds and complexes. It allows direct, simple, and rapid analysis. In most cases no pretreatment of the sample is required. The G.C.-A.A. can be used for direct determinations, to follow the kinetics of a reaction, to screen samples for trace impurities, etc. The only limitation of the G.C.-A.A. is that the metal compound of interest must be volatile at the column temperature.

B. A COMBINED INSTRUMENTAL ANALYSIS TECHNIQUE OF THE FUTURE FOR ELEMENTAL ANALYSIS

The G.C.-A.A. system is a valuable instrumental method of analysis. It offers great potential in speciation studies and in the determination of chemical form. It is necessary to determine the chemical form of heavy metals in order to understand their effects on human health and their environmental impact.

Unfortunately, the G.C.-A.A. system is limited to analysis of samples containing volatile metal compounds which limits it usefulness. A more versatile combined instrumental method of analysis is a liquid chromatograph interfaced to an atomic absorption detector. Liquid chromatography will separate a larger variety of compounds than gas chromatography.

A dual stage carbon furnace atomic absorption detector was designed and built to directly interface to a liquid

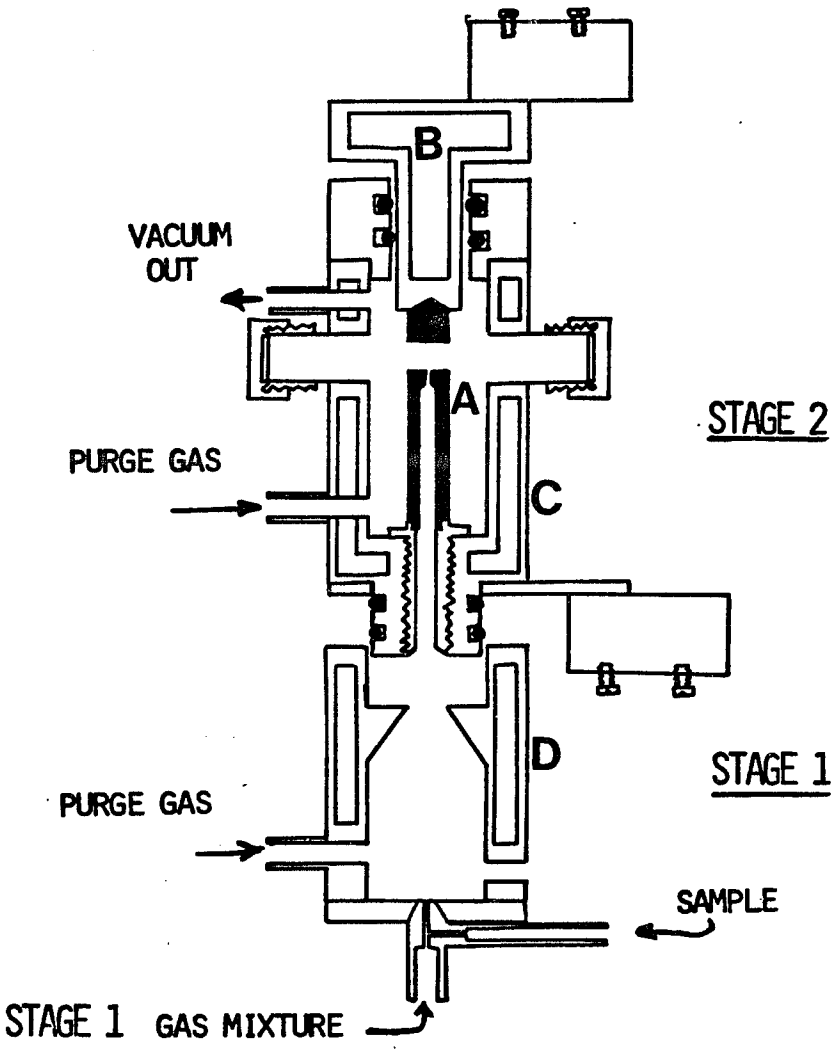
chromatograph (Figure 52). The detector was not demonstrated as part of this dissertation research.

A carbon furnace atomizer was built rather than a conventional flame atomizer because of the increaced sensitivity of carbon furnaces over flame atomizers. An inherent problem with a carbon furnace atomizer as a L.C. detector, however, was its inability to handle large volumes of solvent. For this reason a dual stage atomization system was proposed. The first stage consisted of a flame to initially breakdown the solvent and sample to a form that the second stage carbon atomizer could handle (e.g., CO and H_2 for organic solvents).

The first stage of the atomizer was interchangeable. The flame could be replaced by a wire loop or a resistance heated carbon element depending upon the requirements of the sample being analyzed.

The design of the dual stage atomizer should also allow its direct interface to other separation techniques.

The L.C.-A.A. system will have the great separation potential of L.C. to allow speciation and the sensitivity and selectivity of carbon furnace A.A.



A. Carbon Resistance Element
B. Water-Cooled Electrode
C. Water-Cooled Atomizer Housing
D. Water-Cooled STAGE 1 Housing

FIGURE 52: Schematic Diagram of Dual Stage L.C.-A.A. Detector

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EXAMINATION AND THESIS REPORT

Candidate: Eric Leon Kiesel

Major Field: Analytical Chemistry

Title of Thesis: DEVELOPMENT AND APPLICATIONS OF GAS CHROMATOGRAPHY ATOMIC ABSORPTION INTERFACE INSTRUMENTATION

Approved:

Major Professor and Chairman

Dean of the Graduate School

EXAMINING COMMITTEE:

Date of Examination:

October 30, 1980